Atomic and Molecular Spectroscopy

ATOMIC AND MOLECULAR SPECTROSCOPY

Some important constants:

1. Velocity of light (c) $= 3\times10^{8}$ m/sec $= \dfrac{1}{\sqrt{\mu 0}\,\epsilon_0}$

2. μ_0 (Permeability of free space) $= 4\pi\times10^{-7}$ H/m

$$B = \mu_0 (H + M)$$

3. Permittinity of free space $(\epsilon_0) = 8.86\times10^{-12}$ f/m

4. $\dfrac{1}{4\pi\epsilon_0} = 9\times10^{9}$ coulumb^2/m^2.

5. Planck constant (h) $= 6.6\times10^{-34}$ J$-$s

$$(\hbar) = \frac{h}{2\pi} = 1.05\times10^{-34}\,J-s$$

6. $1\,eV = 1.6\times10^{-19}$ Joule

7. Charge on $e^- = -1.6\times10^{-19}$ coulumb

   Charge on proton $= +1.6\times10^{-19}$ coulumb

8. Rest mass of $e^- = 9.1\times10^{-31}$ kg

   Rest mass of proton $= 1.6726\times10^{-27}$ kg

   Rest mass of neutron $= 1.6749\times10^{-27}$ kg

   Rest mass of neutron $= 1.6749\times10^{-27}$ kg

9. Gravitational constant $(G) = 6.67\times10^{-11}$ Nm^2 / kg^2

10. Avogrado number (N0) $= 6.023\times10^{23}$ molecules / mole

11. Rydberg constant for infinite mass $(R_\infty) = 1.09737\times10^{7}$ / m

12. Bohr radius $(a_0) = 0.53\text{Å} = \dfrac{h^2\,\epsilon_0}{\pi m e^2}$

13. Fine structure constant $(\alpha) = \dfrac{1}{137}$

14. $\dfrac{m_p}{m_e} \approx 1836.15$ $\qquad$ $\dfrac{m_n}{m_e} \sim 1839$

15. Bohr magneton $(\mu_B) = \dfrac{eh}{4\pi m_e} = 9.27\times10^{-24}$ J/T

16. Nuclear magneton $(\mu_N) = \dfrac{eh}{4\pi m_N} = 5.05\times10^{-27}$ J / T

Some important discoveries:

1.	Atom	:	John Dalton
2.	Proton	:	Goldstein
3.	e^-	:	J.J. Thomson
4.	Neutron	:	James Chadwick
5.	Nucleus	:	Rutherford
6.	e^+ (Positron)	:	J-Anderson

Some known facts about the atom:

1. The most part of the atom is hollow p and n lies inside the nucleus while the e^- revolve around nucleus.
2. The atom is neutral while the nucleus is +vely charged.
3. Atom is generally represented by

$${}_{Z}X^{A}$$

Where Z = atomic and A = mass number
In atom, number of protons = number of electrons = Z
and number of neutrons = A-Z

4. Nearly whole mass of the atom (more than 99.9%) is placed at the centre, called nucleus.
5. Atom is taken to be spherical in shape.

Atomic Models:

1. Thomson's atomic model.
2. Rutherford's atomic model.
3. Bohr's atomic model.

(Only for H-atom and one electron ions/atoms such as positronium atom, He^+, Li^{++} etc). According to this model, the electron revolve around the nucleus in circular orbits.

- This model fails to explain the fine structure of the H-atom spectrum and in case of more than one electron systems.

Sommerfeld's atomic model:

Sommerfeld extended the Bohr's model and make the following two corrections.

(a) He considered that the electron revolve around the nucleus in elliptical orbits rather than circular orbit.
(b) He also taken into account the relativistic effect.

Bohr's Atomic Model (For H-atom):

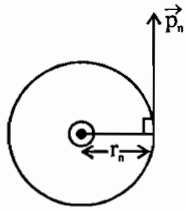
According to it:
(i) Electron revolve around the nucleus in circular orbit.
(ii) Electron revolve around the nucleus only in those orbits in which its angular momentum is an integral multiple of $\frac{h}{2\pi}$,

i.e. $|\bar{L}| = |\bar{r}_n \times \bar{p}_n| = r_n p_n \sin 90° = r_n p_n$

$\therefore \quad r_n p_n = \frac{nh}{2\pi}$

$$mv_n r_n = \frac{nh}{2\pi}$$

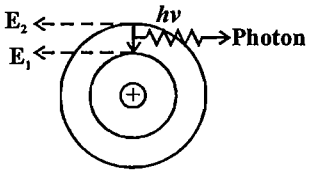
$$\boxed{mV_n r_n = \frac{nh}{2\pi}}$$ where $n = 1, 2, 3, \ldots\ldots\ldots\infty$



(Number of orbits i.e. 1st and 2nd etc.)

(c) When electron gets sufficient energy from outside, it jumps to higher energy state and after some time $(\simeq 10^{-8}\ \text{sec})$, it jumps to lower energy state and emit a photon of energy $h\nu$ which is equal to the difference of energy of two states i.e.

$h\nu = \Delta E = E_2 - E_1$



Energy of photon $= h\nu = E_2 - E_1 = \Delta E$

Bohr's theory of H-atom:

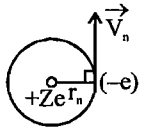
(Energy levels in H-atom):

The required centripetal force to the electron is provided by coulumb force of attraction between the electron and nucleus. Hence,

C.F. = force of attraction (F).

$$\frac{mVn^2}{r_n} = \frac{1}{4\pi\epsilon_0}\frac{(Ze)(e)}{r_n^2}$$

$$\Rightarrow \quad m^2Vn^2r_{n^2} = \frac{1}{4\pi\epsilon_0}Ze^2r_nm$$



$$\left(\frac{nh}{2\pi}\right)^2 = \frac{1}{4\pi\epsilon_0}Ze^2r_nm$$

$$\boxed{r_n = \frac{n^2h^2\epsilon_0}{\pi mZe^2}} \qquad \ldots (1)$$

This expression shows $\boxed{r_n \propto n^2}$ i.e. radius of second orbit is 4 times to that of first orbit $(r_2 = 4r_1)$.

Now, $r_1 = \frac{h^2\epsilon_0}{\pi me^2}$ [For H-atom z=1)

Bohr's radius $= a_0 = 0.53\text{Å} = r_1$ $\qquad r_2 = 4r_1 = 4a_0$

Now, K.E. of electron is $= \frac{1}{2}mV_n^2 = \frac{1}{2}m\left(\frac{nh}{2\pi mr_n}\right)^2$

$$= \frac{1}{2}m \times \frac{n^2h^2}{4\pi^2m^2r_{n^2}}$$

Now putting r_{n^2} from equation, (1) we get

$$\text{K.E.} = \frac{1}{2}m \times \frac{n^2h^2}{4\pi^2m^2}\left(\frac{\pi mZe^2}{n^2h^2\epsilon_0}\right)^2$$

$$\boxed{\text{K.E.} = \frac{me^4z^2}{8\epsilon_0h^2}\left(\frac{1}{n^2}\right)} \qquad \ldots (2)$$

And $P.E. = \frac{1}{4\pi \in_0} \frac{(+Ze)(-e)}{r_n} = -\frac{1}{4\pi \in_0} \frac{Ze^2}{n^2h^2 / \pi mZe^2}$

$$\boxed{P.E. = -\frac{me^4z^2}{4\in_0^2 h^2}\left(\frac{1}{n^2}\right)} \quad \text{... (3)}$$

Now total energy $E_n = K.E. + P.E.$

$$= \frac{-me^4}{8\in_0^2 h^2}\left(\frac{1}{n^2}\right) = \frac{-me^4}{8\in_0^2 ch^3}\frac{hcz^2}{n^2}$$

$$\boxed{E_n = -\frac{R_\infty hcZ^2}{n^2}} \quad \text{... (4)}$$

Where $R_\infty = \frac{me^4}{8\in_0^2 ch^3} = 1.0974 \times 10^7 / m$

For H-atom, $Z = 1$,

$$\therefore \quad \boxed{E_n = \frac{-R_\infty hc}{n^2} = -\frac{13.6\ eV}{n^2}} \quad \text{... (5)}$$

Now, $E_1 = -13.6\ eV$

$E_2 = -3.4\ eV, \qquad E_\infty = 0\ eV$

Therefore, The ionization energy of H-atom $= E_\infty - E_1 = 13.6\ eV$

& Ionization potential = 13.6 eV (There is only one I.P.)

The I[st] excitation energy $= E_2 - E_1 = 10.2\ eV$

- There are infintie number of excitation potential for H-atom.

Now, $E_{n_1} = -\frac{R_\infty hcz^2}{n_1^2}, \ E_{n_2} = -\frac{R_\infty hcz^2}{n_2^2}$

When electron jumps from higher energy state

$n_2 \rightarrow n_1$ (lower), it emits energy = $h\nu$.

$$h\nu = E_{n_2} - E_{n_1} = -\frac{R_\infty hcz^2}{n_2^2} - \left(-\frac{R_\infty hcz^2}{n_1^2}\right)$$

$$h\nu = R_\infty hcz^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad \text{For H-atom, } Z = 1$$

But $\upsilon = \frac{c}{\lambda}$

$$\Rightarrow \quad \boxed{\frac{1}{\lambda} = R_\infty z^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)} \qquad n_1 < n_2$$

For H-atom, $Z = 1$ ... (6)

$$\boxed{\frac{1}{\lambda} = R_\infty\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)} \quad \text{... (7)}$$

Hydrogen spectrum:
(Series of spectrum):

1. **Lyman series:** This series is obtained when the transition of electron occurs (observed in UV region) from $n_2 = 2,3,4.....\infty$ to $n_1 = 1$.

$\therefore$ eqn (7) gives

$$\boxed{\frac{1}{\lambda_{Lyman}} = R_\infty\left(\frac{1}{1^2} - \frac{1}{n_2^2}\right)}$$ where $n_1 = 1$, $n_2 = 2,3,4.....\infty$

The minimum wavelength of lymann series is 912Å and max. $\lambda = 1215$Å.
This is the only series observed in absorption spectra.

2. **Balmer series:** it is observed when the electron jump from $n_2 = 3,4,.....\infty$ to $n_1 = 2$.

$\therefore$ $$\boxed{\frac{1}{\lambda_{Balmer}} = R_\infty\left(\frac{1}{Z^2} - \frac{1}{n_2^2}\right)}$$ where $n_2 = 3,4,.....\infty$

Where $n_2 = 3$, the line observed is H_α

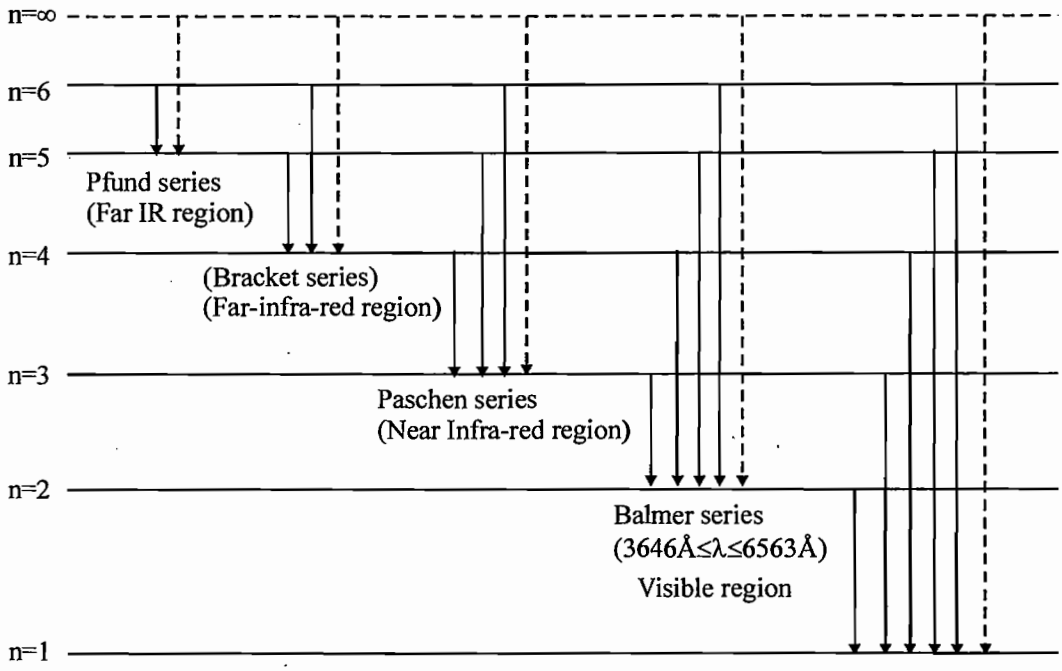
$n_2 = 4$, the line observed is H_β.

Similarly, $H_\gamma, H_\delta,$

Maximum wavelength is of H_α line = 6563 Å.
and min. wavelength = 3646 Å.
This is first series observed for H-atom and is found in visible region.

3. **Paschen series:** Observed in near IR(Infrared)
4. **Brackett-series:** Observed in far IR
5. **Pfund series:** Observed in far IR.

The above series are shown below



(Fig. Hydrogen atom spectrum)

Ionization potential of H-atom:

$$E_n = -\frac{13.6}{n^2}\text{ eV},\ E_1 = -13.6\text{ eV}\ \&\ E_\infty = 0\text{ eV}$$

The ionization potential is defined as the potential which can remove the electron from H-atom. As there is only one electron in H-atom. Hence there is one I.P. for H-atom. Thus the I.P. energy of H-atom.

$$E_\infty - E_1 = 0 - (-13.6\text{ eV}) = 13.6\text{ eV}$$

$\therefore$ I.P. = 13.6 eV

Excitation Potential: There are infinite number of discrete enegy levels in atom. (Franck-Hertz exp.) The excitation energy is defined as the energy acquired to make the electron capable to jump to the higher energy state. The potential corresponding to the excitation energy is known as the excitation potential. There may be infinite number of excitation potential. The first excitation energy when electron is excited from

$$n = 1 \text{ to } n = 2 = -\frac{13.6}{2^2} - \left(-\frac{13.6}{1^2}\right)$$

$$= (-3.4 + 13.6)$$

$$= 10.2\text{ eV}$$

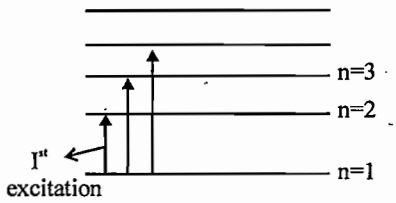


Fig. Different excitation of H-atom

$\therefore$ Ist excitation potential for H-atom = 10.2 V.

- **Variation of the Rydberg constant:** (R_∞)

The Rydberg constant for infinitely heavy nucleus is given as

$$R_\infty = \frac{me^4}{8\epsilon_0^2 ch^3} \qquad \ldots (1)$$

And for nucleus of mass M, $R_M = \frac{\mu e^4}{8\epsilon_0^2 ch^3}$ ... (2)

Where μ = reduced mass,

$$\mu = \frac{mM}{m+M} = \frac{m}{1+\frac{m}{M}}$$

$$\therefore \quad R_M = \frac{me^4}{8\epsilon_0^2 ch^3}$$

$$= \left(\frac{1}{1+\frac{m}{M}}\right)$$

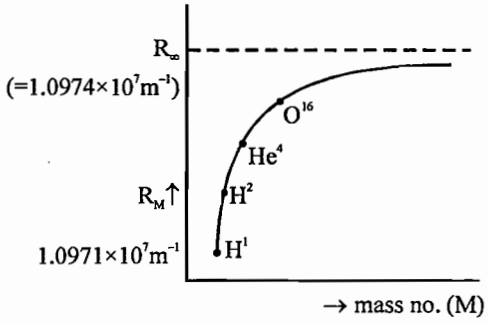


Fig. Variation of Rydberg constant with nuclear mass.

$$\boxed{R_M = \frac{R_\infty}{1+\frac{m}{M}}} \qquad M\uparrow \; R_M \uparrow \text{ (increases)}$$

Energy levels of positronium atom:

In positronium atom an electron revolve around positron (e^+, anti particle of electron)

$$\therefore \qquad E_n = -\frac{R_{positronium}\, hcz^2}{n^2}$$

In this case, $R_{positronium} = \dfrac{R_\infty}{1+\frac{m}{M}} = \dfrac{R_\infty}{2}$ & $z=1$ ... (2)

$$\therefore \qquad \text{Eq(1) gives, } \boxed{E_n = -\frac{R_\infty hc}{2n^2} = -\frac{6.8}{n^2}\text{eV}} \text{ exactly half of H-atom}$$

Thus the I.P. for positronium atom is 6.8 V.

PROBLEMS

1. The lowest series limit wavelength of the Balmer series in H-spectrum is 3646 Å. Calculate the Rydberg constant.

   Ans. $\left(R = 1.097\times10^7\ m^{-1}\right)$

2. If the wavelength of the first line of the Lyman series of hydrogen is 1215Å, calculate the wavelength of the second line of the series and the series limit.

   Ans. 1025Å, 912Å

3. If the wavelength of the Ist line of Balmer series of hydrogen is 6563Å, calculate the I.P. of the atom.

   $\left(h = 6.6\times10^{-34}\ J-s,\ C = 3\times10^8\ m/s\right)$

   Ans. 13.6 V.

4. Calculate the I.P. for He^+, Li^{++} and Positronium atom.

   Ans. 54.4 V, 122.4 V, 6.8 V)

5. How many revolutions does an electron in the n = 2 state of H-atom make before dropping to the n = 1 state? The average life time of an excited state is 10^{-8} sec.

   (Hint: $f = \dfrac{v}{2\pi r_n} = \dfrac{nh/2\pi m r_n}{2\pi r_n} = \dfrac{2R_\infty c}{n^3}$)

   ↓ Classical freq. of revolution

   Ans. 8.2×10^6.

- Find structure of spectrum lines was explained by using Q.M. and also considering the electron-spin motion.The hypothesis of electron-spin was made by Goudsmith and Uhlenbeck and its epxperimental verification was given by stern-Gerlach experiment).

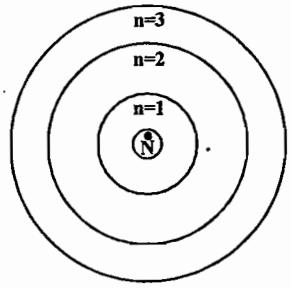
QUANTUM NUMBERS

To determine the position of an electron in an atom, we require the knowledge of following four quantum numbers. These are obtained by using Quantum mechanics and are

1. **Principal quantum number(n):** The principal quantum number tells us about the shell to which a particular electron belongs to n can take the following values.

$n = 1, 2, 3, 4$.....i.e., K, L, M, N,....shells

$n = 1$ or K shell is nearest to the nucleus.



2. **Orbital quantum number or azimuthal quantum number(l):**
This quantum number was introduced by sommerfeld l represents the subshells to which an electron belongs to.
For a given shell (n), l can take the following values.

$\ell = 0, 1, 2.....(n-1)$

Example:
(a) $n = 3$
$\ell = 0 \quad 1 \quad 2$

s-subshell p-subshell d-subshell. Number of subshells in a shell = n.

(b) $n = 1 \quad \ell = 0$ s – subshell only

$n = 2 \quad \ell = 0, 1$ s and p subshells.

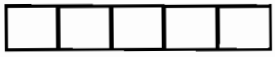
3. **Orbital magnetic quantum number (m_ℓ):** m_ℓ represents the different states corresponding to a subshell (l).

m_ℓ can take the values given as

$m_\ell = \ell, (\ell-1).....1, 0, -1, -2....(-\ell)$

Example: If $\ell = 2$ (d-subshell)

$m_\ell = 2, 1, 0, -1, -2$ (Total 5 values)



4. **Magnetic spin quantum number (m_s):**

m_s represents the oriantation of an electron in an state for an electron for spin 1/2, m_s can take the values,

$m_s = +\frac{1}{2}, \quad -\frac{1}{2}$ For $s = \frac{1}{2}$

$\uparrow \quad \downarrow$ $m_s = -s$ to $+s$

(Orientation in +z direction) (Orientation in – z direction) with difference 1

The order of filling of an electron in different subshell is given below.

$(Is^2)\ (2s^2\ 2p^6)\ (3s^2\ 3p^6\ 3d^{10})\ (4s^2\ 4p^6)$ ..... But

Correct $\rightarrow (1s)^2\ (2s^2 2p^6)\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}$.....

(We see $n+\ell$ values, more $(n+\ell)$ value energy will be more; if $(n+l)$ is same for two subshell the energy of higher n subshell is more. This is why 4s is after 3p as for

$4s\ (n+\ell=4+0)$ & $3p(n+\ell=3+1)$

- 3f does not exists as for $\overset{n}{\uparrow}\overset{\ell}{\uparrow}3f = n=3$ & $\ell=3$ and $\ell=3$ is not possible for $n=3$.
- Max. electrons in s, p, d, f, g, h ..... subshells are 2, 6, 10, 14, 18, 22 ..... respectively.
- Total number of electrons in a shell n is $\boxed{2n^2}$.

$=2\times$ total m_ℓ values for a given n.

$$=2\times\sum_{\ell=0}^{n-1}2\ell+1=2\times\sum_{\ell=0}^{n-1}(2\ell+1)$$

$$=2\times\left[1+3+5....+(2n-1)\right]=2n^2$$

- Max. electrons in an outermost shell is 8.
(Except $n=1$ in which only 2 max. electron can live)
- As atom is very small in size i.e. micro system so most of the problems related with atom are solved by quantum Mechanics. In quantum mechanics, any system is represented by a wave function (ψ) which provide every information regarding the system.

$(\psi \rightarrow$ Schrodinger wave function$)$

- The wave funcion which represents the different states of an atom is given by

$\psi_{n,\ell,m_\ell}(r,\theta,\phi)$; r,θ,ϕ are spherical. Co-ordinates as the shape of the atom is spherical. But electron of an atom are revolve around nucleus in elliptical orbits/Circular orbits.

- For $n=2$, the different states of the atom are obtained as

$$n=2,\ \ell=0;\ 1 \qquad \left(E_n=-\frac{13.6}{n^2}eV\right)$$

$m_\ell=0,-1,0,+1$

$\therefore$ The total states are $\psi_{200},\psi_{210},\psi_{21\bar{1}},\ \psi_{211}$ for H-atom, the energy of all these four states is $-\frac{13.6}{2^2}=3.4$ eV as $n=2$ for all these four states.

Thus the level $n=2$ is four feld degenerate or we can say that the degeneracy of $n=2$ level is 4. (Total m_ℓ valeus)

Thus, for a level n, the degeneracy of a level is

$=$ Total m_ℓ values.

$$=\sum_{\ell=0}^{n-1}(2\ell+1)=1+3+5....+(2n-1)$$

$$=n^2$$

- If we include spin degeneracy becomes doubled i.e. zn^2.
- By the term degeneracy we mean, the total number of states which have the same energy?
- The fine structure of lineswas explained by including spin of electron.
- In fine structure, The degeneracy of a level is removed.
- Pauli exclusion principle states "no two electrons in an atom can have all four quantum number same."
- The valence optical electrons are the outermost shell electrons in an atom.

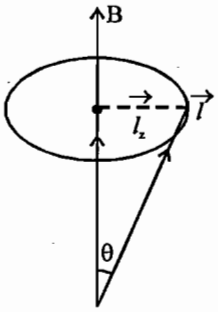
$n = 3$

$\ell = 0,1,2$ $\qquad$ $3p \Rightarrow n = 3,\ \ell = 1$

$m_\ell = 0,(-1,0,1),(-2,-1,0,1,2)$

Space Quantization of an atom:

The orientation of $\vec{\ell}$ in space is quantised (Discrete).



$\vec{\ell}_z = \vec{\ell}\cos\theta$

$|\vec{\ell}_z| = m_e\hbar$ & $|\vec{\ell}| = \hbar\sqrt{\ell\ell+1}$

$$\Rightarrow \qquad \cos\theta = \frac{|\vec{\ell}_z|}{|\vec{\ell}|} = \frac{m_\ell\hbar}{\hbar\sqrt{\ell(\ell+1)}}$$

$$\boxed{\cos\theta = \frac{m_\ell}{\sqrt{\ell(\ell+1)}}}$$

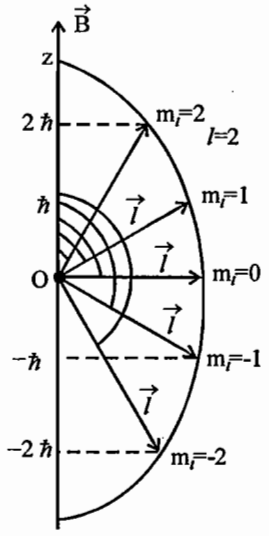
For a given ℓ; $m_\ell = -\ell,(-\ell+1).....,(\ell-1),(\ell)$

Since, $\qquad \sqrt{\ell(\ell+1)} > m_\ell$

$$\Rightarrow \qquad \frac{m_\ell}{\sqrt{\ell(\ell+1)}} < 1$$

$\Rightarrow \qquad \cos\theta \neq 1 \qquad \Rightarrow \qquad \theta \neq 0$

i.e. $\vec{\ell}$ can never be in direction of $\vec{\ell}_z$ or $\vec{B}$ or in z-direction.



Example: If $\ell = 2$, $\quad m_\ell = -2,-1,0,1,2$

$|\vec{\ell}| = \hbar\sqrt{\ell(\ell+1)}$ $\qquad$ $|\vec{\ell}| = \ell\cos\theta$

$= m_\ell\hbar$

It gives,

$$\cos\theta = \frac{-2}{\sqrt{6}}, \frac{-1}{\sqrt{6}}, 0, \frac{1}{\sqrt{6}}, \frac{2}{\sqrt{6}}, \text{ for } l=2$$

Vector model of atom:

We have that orbital angular momentum.

$$\boxed{|\vec{\ell}| = \hbar\sqrt{\ell(\ell+1)}} \qquad \ldots (1)$$

$\boxed{|\vec{\ell}_z| = m_\ell \hbar}$; $m_\ell = -\ell$ to $+\ell$ with zero

Similarly, spin angular momentum:

$$\boxed{|\vec{s}| = \hbar\sqrt{s(s+1)}} \qquad \ldots (2)$$

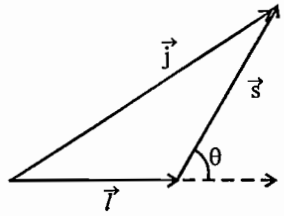
& $|\vec{s}_z| = m_s \hbar$ $\qquad m_s = \pm\frac{1}{2} = \pm s$

Where s is spin quantum number $= +\frac{1}{2}$

Now the total angular momentum

$\vec{j} = \vec{\ell} + \vec{s}$

$$\therefore \quad \boxed{|\vec{j}| = \hbar\sqrt{j(j+1)}} \qquad \ldots (3)$$



$|\vec{j}_z| = m_j \hbar$

Where $m_j = -j, -j+1, j+2, \ldots, j-1, +j$

- The stern-Gerlach exp. give an experimental evidence of electron spin and directly demonstrate space quantization of atom and verify the salient features or vector atom model.
- **Angle between $\vec{\ell}$ and $\vec{s}$:**

$$\vec{j} = \vec{\ell} + \vec{s}$$

$$\boxed{\vec{j} = \vec{\ell} + \vec{s}}$$

$$\therefore \quad \vec{j}.\vec{j} = (\vec{\ell} + \vec{s}).(\vec{\ell} + \vec{s}) = |\vec{\ell}|^2 + |\vec{s}| + 2\vec{\ell}.\vec{s}$$

$$\Rightarrow \quad 2\vec{\ell}.\vec{s} = |\vec{j}|^2 - |\vec{\ell}|^2 - |\vec{s}|^2$$

$$\Rightarrow \quad 2|\vec{\ell}||\vec{s}|\cos\theta = |\vec{j}|^2 - |\vec{j}|^2 - |\vec{s}|$$

$$\boxed{\cos\theta \text{ or } \cos(\vec{\ell}.\vec{s}) = \frac{j(j+1) - \ell(\ell+1) - s(s+1)}{2\sqrt{\ell(\ell+1)}\sqrt{s(s+1)}}}$$

Angle between $\vec{j}$ & $\vec{\ell}$:

As $\vec{j} = \vec{\ell} + \vec{s}$

$$\Rightarrow \quad \vec{s} = \vec{j} - \vec{\ell}$$

$$\Rightarrow \quad \vec{s}.\vec{s} = (\vec{j} - \vec{\ell}).(\vec{j}.\vec{\ell})$$

$$\Rightarrow \quad |\vec{s}|^2 = |\vec{j}|^2 + |\vec{\ell}|^2 - 2\vec{j}.\vec{\ell}$$

$$\Rightarrow \quad 2\vec{j}.\vec{\ell} = |\vec{j}|^2 + |\vec{\ell}|^2 - |\vec{s}|^2$$

$$\Rightarrow \quad \boxed{\cos\theta = \cos(\vec{j}.\vec{\ell}) = \frac{j(\vec{j}+\ell) + \ell(\ell+1) - s(s+1)}{2\sqrt{j(j+1)}\sqrt{\ell(\ell+1)}}}$$

Angle between $\vec{j}$ & $\vec{s}$:

$$\Rightarrow \quad \vec{\ell} = \vec{j} - \vec{s}$$

$$\Rightarrow \quad \vec{\ell}.\vec{\ell} = \left(\vec{j} - \vec{s}\right).\left(\vec{j} - \vec{s}\right)$$

$$\Rightarrow \quad \left|\vec{\ell}\right|^2 = \left|\vec{j}\right|^2 + \left|\vec{s}\right|^2 - 2\vec{j}.\vec{s}$$

$$\Rightarrow \quad 2\vec{j}.\vec{s} = \left|\vec{j}\right|^2 + \left|\vec{s}\right|^2 - \left|\vec{\ell}\right|^2$$

$$\Rightarrow \quad 2\left|\vec{j}\right|\left|\vec{s}\right|\cos\theta = \left|\vec{j}\right|^2 + \left|\vec{s}\right|^2 - \left|\vec{\ell}\right|^2$$

$$\boxed{\cos\theta = \cos\left(\vec{j}.\vec{s}\right) = \frac{j(j+1)+s(s+1)-\ell\ell+1}{2\sqrt{j(j+1)}\sqrt{s(s+1)}}}$$

- For electron total angular momentum, orbital angular momentum and spin angular momentum are denoted by $\vec{j}$, $\vec{\ell}$ & $\vec{s}$ respectively. While for atom or for a system of two or more electron, these are denoted by $\vec{J}$, $\vec{L}$ & $\vec{S}$ respectively.

For one electron (system) atom.

$\vec{j} = \vec{J}$, $\vec{\ell} = \vec{L}$ & $\vec{s} = \vec{S}$

MAGNETIC DIPOLE MOMENTS, ELECTRON SPIN AND VECTOR ATOM

- Orbital magnetic dipole moment of electron:

$M_\ell = NiA$ for one turn N = 1 $\Rightarrow$ $M_\ell\ iA$

Let a is the radius of the orbit in which electron is moving. Now current:

$$i = \frac{e}{T} \qquad \ldots (1)$$

where e = charge of electron and T = time period.

Let v = velocity of the electron.

$$\therefore \quad T = \frac{2\pi a}{v} \qquad \ldots (2)$$

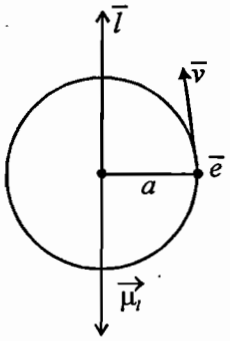
Putting (2) in (1), we get

$$i = \frac{ev}{2\pi a}$$

Now magnitude of orbital magnetic dipole moment $\left(\vec{\mu}_\ell\right)$.

$$\left|\vec{\mu}_\ell\right| = iA = \frac{ev}{2\pi a} \times \pi a^2 = \frac{eva}{2} \qquad \ldots (3)$$

Also $\left|\vec{\ell}\right|$ = magnitdue of the orbital angular momentum = mva ... (4)



Now 3/4 gives;

$$\left|\frac{\vec{\mu}_\ell}{\vec{\ell}}\right| = \frac{e}{2m} = \text{constant} \qquad \ldots (5)$$

(=gyromagnetic ratio of the electron)

In vector form, $\vec{\mu}_\ell = \frac{-e}{2m}\vec{\ell}$ or $\vec{\mu}_\ell = -g_\ell \frac{e}{2m}\vec{s}$ $\Rightarrow$ $g_\ell = 1$

g_ℓ = orbital g-factor

Similarly, spin magnetic moment,

$$\vec{\mu}_s = -g_s \frac{e}{2m}\vec{s} = \frac{-e}{m}\vec{s}$$

$g_s = 2$

Where g_s = spin g-factor.

And Total magnetic moment

$$\vec{\mu}_J = -g_j \frac{e}{2m}\vec{J}$$

$$g_J = 1 + \frac{J(J+1) + s(s+1) - L(L+1)}{2J(J+1)}$$

Where J = Lande g-factor.

Stern-Gerlach Experiment:

Stern and Gerlach, in 1921, perfomed an experiment which demonstrated directly that an atom placed in a magnetic field can take only certain discrete orientations with respect to the field (space quantisation). It also demonstrated the existence of electron spin, thus providing an experimental verification of the vector model of atom.

The plan of the experiment is shown in fig. A beam of neutral silver atoms was formed by heating silver in an oven. It was collimated by a few fine slits and then passed.

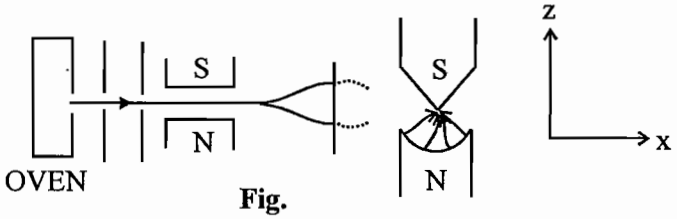


Fig.

through a non-homogeneous magnetic field. The beam leaving the mgnetic field was received on a photo-graphic plate P.

Let us consider the experimental results quantitatively. The average transverse force experienced by an atomic magnet traversing the (inhomogenous) magnetic field is:

$$F = -\frac{\partial U}{\partial z} = \mu_{J_z} \frac{\partial B}{\partial z} = \mu_J$$

$$\left\{\begin{array}{l} U = -\bar{\mu}_J . \bar{B} \\ \text{As} = -\mu_J B \cos\theta \\ \quad = -\mu_{J_z} B \end{array}\right\}$$

Where $\partial B_z / \partial z$ is the rate of change of field in the z-direction, and μ_{jz} is the z-component of the total (orbital+spin) magnetic moment $\vec{\mu}_J$ of the atom. The relation between the total magnetic dipole moment and the total angular momentum $\vec{J}$ is:

$$\vec{\mu}_j = -g_j \left(\frac{e}{2m}\right)\vec{J}$$

$$= -g_j \left(\mu_B \frac{2\pi}{h}\right)\vec{J}.$$

Where g_j is the corresponding g factor, and $\mu_B = (= e\,h / 4\pi m)$ is Bohr magneton. The possible components of $\vec{\mu}_j$ along z-axis are given by

$$\mu_{Jz} = -g_j \left(\mu_B \frac{2\pi}{h}\right)\left|\overrightarrow{J_z}\right|$$

$$= -g_j \left(\mu_B \frac{2\pi}{h}\right) m_j \frac{h}{2\pi}$$

$$\mu_{J_z} = -g_j \mu_B m_j$$

where the magnetic quantum number m_j can assume a total of $(2j+1)$ values ranging from +j to –j. Thus

$$F_z = \frac{\partial B_z}{\partial z} g_j \mu_B m_j$$

Because of this force the atoms (mass M) have a transverse acceleration a_z given by

$$a_z = \frac{F_z}{M} = \frac{1}{M}\frac{\partial B_z}{\partial z} g_j \mu_B m_j$$

If v_x be the longitudinal velocity of the atoms and d be the length of their path in the magnetic field, then the time t for which they experience the transverse force is:

$$t = \frac{d}{\mathrm{v}_x}$$

But, from kinetictheory, the velociy v_x of an atom of mass M is evaluate by setting

$$\frac{1}{2} M \mathrm{v}_x^2 = 2kT^*$$

where k is Boltzmann constant and T is kelvin temperature of the oven. From this, we have

$$\mathrm{v}_x = \sqrt{\frac{4kT}{M}}$$

and so $$t = \frac{d}{\mathrm{v}_x} = d\sqrt{\frac{M}{4kT}}$$

Therefore, the transvese deflection suffered by the atoms is given by

$$Z = \frac{1}{2} a_z t^2$$

$$= \frac{1}{2}\left(\frac{1}{M}\frac{\partial B_z}{\partial z} g_j \mu_B m_j\right) d^2 \left(\frac{M}{4kT}\right)$$

$$Z = g_j m_j \frac{\frac{\partial B_z}{\partial z}\mu_B d^2}{8kT}$$

- **Calculation of spectroscopic terms:** Spectroscopic term is one, where electron in an atom is more probably live.

The spectroscopic terms are determined as

$$\boxed{n.^{2s+1}L_J^P}$$

Here n = principal quantum number
s = spin quantum number
L = Orbital quantum number
J = Total angular quantum number

& P stands for parity. If the spectroscopic term is obtained for a system of odd electronic configurtion. We write 'O' and for even electronic configuration we don't write anything (The odd and even configuration is determined by the total l values).

If L = 0, S state ; L = 1, P state; L =2, D state etc.

Problem: Determine the possible term of a one electron atom corresponding to n = 3 and compute the angle between $\vec{\ell}$ & $\vec{s}$ for the term $^2D_{5/2}$.

Soln. n = 3 $\quad \ell = 0,1,2 \quad$ $J = \ell + s$

one electron $\quad s = 1/2$

When $\ell = 0, s = 1/2 \Rightarrow J = 1/2 \Rightarrow$ The spectroscopic term $^2S_{1/2}$

$$\ell = 1; s = \frac{1}{2} \Rightarrow J = 1/2, 3/2 \Rightarrow {}^2P_{1/2}, {}^2P_{3/2}$$

$$\ell = 2; s = \frac{1}{2} \Rightarrow J = \frac{3}{2}, \frac{5}{2} \Rightarrow {}^2D_{3/2}, {}^2D_{5/2}$$

For the term $^2D_{5/2}$, the angle between $\vec{\ell}$ & $\vec{s}$ is given as

$$\cos\theta = \frac{J(J+1) - \ell(\ell+1) - s(s+1)}{2\sqrt{\ell(\ell+1)}\sqrt{s(s+1)}} \qquad \underbrace{S = \frac{1}{2}, L = 2, J = \frac{5}{2}}_{\downarrow\ {}^2D_{5/2}}$$

$$= \frac{5/2(5/2+1) - 2(2+1) - \frac{1}{2}\left(\frac{1}{2}+1\right)}{2\sqrt{6}\sqrt{3/4}} = 0.4714$$

$$\theta = \cos^{-1}(0.4714)$$

$$= 61.9°$$

Formula for finding parity $=(-1)^{\ell}$ $=+$ve or even If $\ell =$ even or 0

$-$ ve or odd If ℓ=odd

Problem: ${}^{1}S_0$ is right or wrong ${}^{2s+1}L_J^P$

$1=2s+1 \qquad s=0$

$L=0$

$J=0$, This is right.

$\Rightarrow \quad {}^{2}D_{5/2}$

$2=2s+1 \quad s=\frac{1}{2}, \; L=2, \; J=5/2$ right

${}^{2}D_{7/2}$ is wrong

- **Various types of coupling:**

There are two types of coupling, arises due to three kind of interactions viz. spin-spin correlation orbital-orbital interaction (residual electrostatic interaction) and spin-orbit interaction. There are

(i) L-S coupling (in lighter atoms)

(ii) j-j coupling (in heaviour atoms)

(i) **L-S coupling:** This is also known as Russel-Saunder's coupling. This type of coupling happens in lighter atoms. In this coupling, spin-spin correlation and orbital-orbital interaction is stronger in comparision of spin-orbit interactions. It is divided into three steps:

(a) **Spin-spin correlation:** Due to this stronger interaction, the spin angular momentum of individual optical electrons combines to give a resultant spin angular momentum $(\vec{S})$, given as

$$\vec{S}=\vec{S}_1+\vec{S}_2+\vec{S}_3+.....$$

The magnitude of resultant spin, angular momentum $\vec{S}$ is given by $|\vec{S}|=\hbar\sqrt{S(S+1)}$

Where the total spin quantum number (s) can take the values.

$S=|s_1+s_2+....|_{min}, \; |s_1+s_2+....|_{min}+1, ...(s_1+s_2+.....)$

Example: For one electron $S=s_1=\frac{1}{2}$ (doublet as 2s+1=2)

For two electron $s_1=\frac{1}{2}, s_2=\frac{1}{2}$

$\Rightarrow \quad S=|s_1-s_2|.....(s_1+s_2)$

$=0,1$ (singlet, triplets)

For three electrons $\rightarrow$ $s_1=\frac{1}{2}, \; s_2=\frac{1}{2}, \; s_3=\frac{1}{2}$

$s'=0, 1$

$S=\frac{1}{2}, \frac{1}{2}, \frac{3}{2}$ (Two doublets & one quartets)

In general,

1. For N even $e^- \rightarrow$ $S = 0, 1, 2 \ldots\ldots N/2$

2. For N odd $e^- \rightarrow$ $S = \frac{1}{2}, \frac{3}{2}, \frac{5}{2} \ldots\ldots \frac{N}{2}$

OR

For one electron $\rightarrow$ $S = s_1 = ½$ (doublet)

For two electrons $\rightarrow$ S=0 (Singlet) S=1 (Triplet)

For three electron $\rightarrow$ S = ½ (doublet) S = ½ (doublet) S = 3/2 (doublet)

For four $e^- \rightarrow$ S=0 (Singlet) S=1 (Triplet) S=0 (Singlet) S=1 (Triplet) S=0 (Singlet) S=1 (Triplet)

(b) Residual electrostatic interaction: As a result of this stronger interaction, the orbital angular moment of individual electrons coupled to give the resultant orbital angular momentum $\vec{L}$, given as:

$\vec{L} = \vec{\ell}_1 + \vec{\ell}_2 + \vec{\ell}_3 + \ldots\ldots\ldots$

of magnitude given by, $|\vec{L}| = \hbar\sqrt{L(L+1)}$

Where L is known as total orbital angular momentum quantum number and it is given as

$L = |\vec{\ell}_1 + \vec{\ell}_2 + \ldots\ldots|_{min}, \ |\vec{\ell}_1 + \vec{\ell}_2 + \ldots\ldots|_{min} + 1, \ \ldots\ldots(\ell_1 + \ell_2 + \ldots\ldots)$

Example: For electron in 2p $\rightarrow$ $\ell_1 = 1 = L$ $(P \text{ state})$

For electrons in 3p 3d $\rightarrow$ $\ell_1 = 1, \ \ell_2 = 2$

$\Rightarrow$ $L = (2-1)\ldots\ldots(2+1)$

$= 1, 2, 3$ $(P, D, F \text{ state})$

For electrons in 2p 3p 3d $\rightarrow$ $l_1 = 1$ $l_2 = 1$ $l_3 = 2$

$L' = 0, 1, 2$

$L'=0$, $l_3=2$] L=2 (D state)

$L'=1$, $l_3=2$] L=1,2,3 (P,D,F states)

$L'=2$, $l_3=2$] L=(0,1,2,3,4) (S,P,D,F,G states)

(c) Spin-orbit interaction: As a result of this week interaction, the resultant $\vec{S}$ & $\vec{L}$, couples less strongly to give total resultamt angular momentum $(\vec{J})$ given by

$\vec{J} = \vec{L} + \vec{S}$

of magnitude $|\vec{J}| = \hbar\sqrt{J(J+1)}$

Where total angular momentum Quantum number J is given as

$$J = |L-S|_{min} \quad |L-S|_{min}+1 \ldots\ldots (L+S)$$

(ii) **j-j coupling:** This coupling is just opposite to thah of L–S coupling. It happens in heavier atoms. In it spin-orbit interaction is relatively stronger than spin-spin correlation and redisual electrostatic interaction. It happens in the following steps:

(a) Spin-orbit interaction: As a result of this relatively stronger interaction the spin angular momentum of individual electrons combine with the orbital angular momentum to give the resultant angular momentum vectors $\vec{j}_1, \vec{j}_2 \ldots\ldots$

$\vec{j}_1 = \vec{\ell}_1 + \vec{s}_1, \vec{j}_2 = \vec{\ell}_2 + \vec{s}_2, \ldots\ldots\ldots$

Where $|\vec{j}_1| = \hbar\sqrt{j_1(j_1+1)}$ & $j_1 = \ell_1 \pm s_1 = \ell_1 \pm \frac{1}{2}$

(b) **Spin-spin correlation and residual electrostatic interaction:**

As a result of these weaker interactions, $\vec{j}_1, \vec{j}_2, \ldots\ldots$ combines to give the total resultant angular momentum $\vec{J}$ given by:

$\vec{J} = \vec{j}_1 + \vec{j}_2 + \ldots\ldots\ldots$

of magnitude $|\vec{J}| = \hbar\sqrt{J(J+1)}$

And $J = |\vec{j}_1 + \vec{j}_2 + \ldots\ldots\ldots|_{min}, |\vec{j}_1 + \vec{j}_2 + \ldots\ldots|_{min} + 1, \ldots\ldots (j_1 + j_2 + \ldots\ldots\ldots)$

J is total angular momentum Q.NO.

Example: For 4p 4d electrons: $\ell_1 = 1, S_1 = \frac{1}{2} \Rightarrow j_1 = \frac{1}{2}, \frac{3}{2}$ for p electron

$$\ell_2 = 2, S_2 = \frac{1}{2} \qquad \Rightarrow \qquad j_2 = \frac{3}{2}, \frac{5}{2} \text{ for D electron}$$

Now (j_1, j_2) gives J

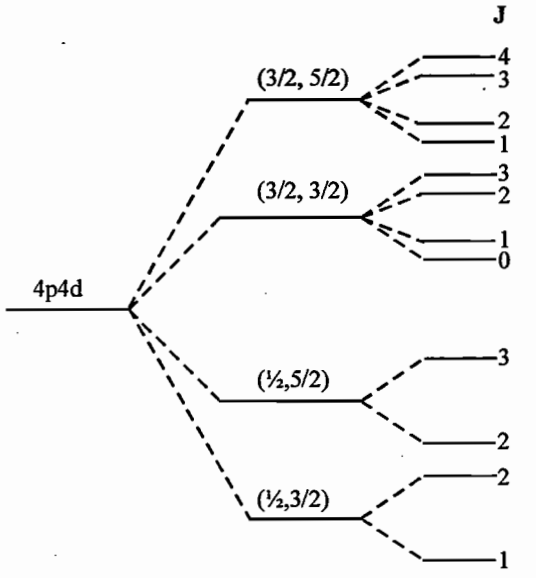
Values of j_1 & j_2 has 4 possible (j_1, j_2) combinations

$\Rightarrow$ $\left(\frac{1}{2}, \frac{3}{2}\right)$ gives J=1,2

$\left(\frac{1}{2}, \frac{5}{2}\right)$ gives J=2,3

$\left(\frac{3}{2}, \frac{3}{2}\right)$ gives J=0,1,2,3

$\left(\frac{3}{2}, \frac{5}{2}\right)$ gives J=1,2,3,4



Unperturbed Level = Spin-orbit interaction + spin-spin correlation & residual electrostatic interaction

- **Determination of spectral terms under L-S coupling:**

Since the core electrons do not contribute to the angular momentum of the atom. We must consider only the (optical) electron outside the completed subshell for completed subshell for computing the term. We can divide the various atoms into three categories:

(i) Atom with one optical electrons:

For a hydrogen like atom ground state configuration is 1s for this we have

$$\Rightarrow \quad S_1 = \frac{1}{2},\ \ell_1 = 0$$

So, that $S = s_1 = \frac{1}{2}$

Multiplicity $\left(2\times\frac{1}{2}+1\right) = 2$ (doublet)

$L = \ell_1 = 0$ (S-slate)

and $j = |L-S|,.....|L-S|+1.....(L+S)$

$= \frac{1}{2}$

Thus the ground state term of H-atom is ${}^2S_{1/2}$. The ground state configuration of an alkali atoms Li, Na, K etc which have optical electron and electronic configuration $(n-1)s^2p^6ns^1$. The ground state term is ${}^2S_{1/2}$.

The excited state configuration and corresponding term for a H like atom would be

$2s, 3s, 4s.....$ ${}^2S_{1/2}$

$2p, 3p, 4p.....$ ${}^2p^0_{1/2}$, ${}^2p^0_{3/2}$ or ${}^2p^0_{1/2,3/2}$

$3d, 4d.....$ ${}^2D_{3/2}$, ${}^2D_{5/2}$

2. Atoms with two or more non-equivalent optical electrons:

Let us consider an atom having optical electrons with outer configuration (2s 2p), (3s 4s) (3s, 4p)

- (In this, n & ℓ are not same, one of them is different or both are different).

Let us calculate terms for $\boxed{2p\ 3d}$

For this we have $S_1 = \frac{1}{2}, S_2 = \frac{1}{2}, \ell_1 = 1, \ell_2 = 2$ the possible value of S & L are

$S = |S_1 - S_2|, |S_1 - S_2| + 1 \ldots\ldots (S_1 + S_2)$

$S = 0, 1$

multiplicity $= (2s+1) = 1, 3 (\text{singlet, triplet})$

and $L = |\ell_1 - \ell_2|, |\ell_1 - \ell_2| + 1 \ldots\ldots\ldots |\ell_1 + \ell_2|$

$L = 1, 2, 3 \quad (P, D, F \text{ states})$

All the terms are odd because the configuration 4p 4d is odd $(\Sigma \ell = 1 + 2 = 3)$

Now for singlets terms we have $\begin{cases} S = 0, & J = 1 \\ L = 1 \end{cases}$

$\Rightarrow$ term $^1P_1^0$

$\begin{cases} S = 0, \ j = 2 \\ L = 2 \end{cases} \Rightarrow$ term $^1D_2^0$

& $\begin{cases} S = 0, \ j = 3 \\ L = 3 \end{cases} \Rightarrow$ term $^1F_3^0$

For triplet terms, we have

$\begin{cases} S = 1, \ j = 0, 1, 2 \\ L = 1 \end{cases} \Rightarrow$ term $^3p_0^0, 3p_1^0, 3p_2^0$

$\begin{cases} S = 1, \ j = 1, 2, 3 \\ L = 2 \end{cases} \Rightarrow$ term $3D_1^0, 3D_2^0, 3D_3^0$

$\begin{cases} S = 1, \ j = 2, 3, 4 \\ L = 3 \end{cases} \Rightarrow$ term $3F_2^0\ 3F_3^0\ 3F_4^0$

For practise, certain outer electrons configurtion and their term are given in table.

Electronic configuration:

1. SS $\rightarrow$ $^1S_0,\ ^3S_1$
2. SP $\rightarrow$ $^1P_1^0,\ ^3P_{0,1,2}^0$
3. SD $\rightarrow$ $^1D_2, ^3D_{1,2,3}$
4. PP $\rightarrow$ $^1S_0, ^1P_1, ^1D_2, ^3S_1, ^3P_{0,1,2}, ^3D_{1,2,3}$
   $^3D_{1,2,3}, ^3F_{2,3,4}, ^3G_{3,4,5}$

(i) **For SS →** $S_1 = \frac{1}{2}, S_2 = \frac{1}{2}, \ell_1 = 0, \ell_2 = 0$

$S = 0,1$ multiplicity $(2s+1) = 1,3$ (singlet triplet)

For singlet → $s = 0, \quad J = 0$

$L = 0$

For triplet $s = 1, \quad J = 1$

$L = 0$ term ${}^3s_1$

(ii) **For SP:** $s_1 = \frac{1}{2}, s_2 = \frac{1}{2}, \ell_1 = 0, \ell_2 = 1$

$s = 0,1, \qquad j = 0,1,2$

term ${}^1p_0^1$

For triplet $s = 1 \quad J = 0,1,2$

$L = 1$ term ${}^3p_{0,1,2}^0$

(iii) **For SD:** $s_1 = \frac{1}{2}, s_2 = \frac{1}{2}, \ell_1 = 0, \ell_2 = 2$

$s = 0,1$

$L = 2$

For singlet $s = 0, \quad J = 2$

$L = 2$ term ${}^1D_2$

For triplet $s = 1 \quad J = 1,2,3$

$L = 2$ term ${}^3D_1, {}^3D_2, {}^3D_3$

OR

terms are ${}^1D_2, {}^3D_{1,2,3}$

(iv) **For PP:** $s_1 = \frac{1}{2}, s_2 = \frac{1}{2}, \ell_1 = 1, \ell_2 = 1$

$S = 0,1$

$L = 0,1,2$

For singlet $\begin{cases} S = 0 \\ L = 0 \end{cases}, \quad J = 0$

term ${}^1S_0$

$\begin{cases} S = 0 \\ L = 1 \end{cases}, \quad J = 1$ term ${}^1p_1$

$\begin{cases} S = 0 \\ L = 2 \end{cases}, \quad J = 2$ term ${}^1D_2$

For triplet $\begin{cases} S = 1 \\ L = 0 \end{cases}, \quad J = 1$

term ${}^3S_1$

$$\begin{cases} S=1 \\ L=1 \end{cases}, \qquad J=0,1,2 \qquad \text{term } {}^3p_0, {}^3p_1, {}^3p_2$$

$$\begin{cases} S=1 \\ L=2 \end{cases}, \qquad J=1,2,3$$

$$\text{term } {}^3D_1, {}^3D_2, {}^3D_3$$

Similarly, we can determine the spectroscopic terms for three or more non-equivalent electrons.

3. **Atoms with two or more equivalent electrons:**

For two equivalent electrons (same n and l values for both or more electrons) the values atleast one of the remaining Q.No. $(m_\ell$ or $m_s)$ must differ to satisfy Pauli exclusion principle. Hence certain terms which were possible for two or more non equivalent electrons are now not possible here. Before the determination of terms we must discossed two important factors:

(i) A closed subshell such as s^2, p^6, d^{10}, f^{14} always form a ${}^1S_0$ term only since for them:

$$\Sigma m_\ell = 0$$

$$\Sigma m_s = 0$$

This means that $M_L = 0, \; M_s = 0$

and so, $L=0, S=0 \Rightarrow J=0 \rightarrow {}^1S_0$

(s-state) (singlet)

$\therefore$ J = 0, i.e. the only possible term is ${}^1S_0$. Hence, we conclude that when a subshell is completely filled the only allowed state is one in which the total spin angular momentum. Total orbital angular momentum and total angular momentum all are zero and hence no magnetic moment.

(ii) The term of configuration $(n\ell)^q$ are the same as the terms of the configuration $(n\ell)^{r-q}$ where r is the max. numbers of electrons i.e. $2(2\ell+1)$.

Example:

Terms for p^5 the same as those of $p^{6-5} = p^1$, term

Terms fo p^4 the same as those of $p^{6-4} = p^2$, the term

Terms fo d^8 the same as those of d^2 and so on.

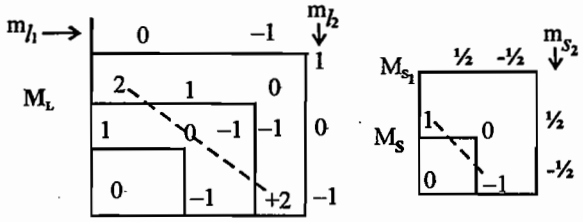
- **Calculation of spectroscopic term for p^2:**

Here $\left.\begin{matrix} \ell_1 = 1; \; s_1 = \frac{1}{2} \\ \ell_2 = 1; \; s_2 = \frac{1}{2} \end{matrix}\right] \Rightarrow L = 0,1,2 \;\&\; S = 0,1$

For the calculation of spectroscopic terms in case of equivalent electrons, we have to consider the Pauli's exclusion principle i.e the four quantum number $(n, \ell, m_l \;\&\; m_s)$ should not be same for any two electrons in an atom for the calculation of spectroscopic terms in case equivalent electrons we use the Breit-Scheme which is follows as:

Breit scheme for possible M_L-values is:

(i) For s=1



We take

Only L = 1

We have to leave the diagonal values for the validity. Since of Pauli's exclusion principle

$\therefore \quad J = 0,1,2$

$\therefore$ terms are ${}^3p_{0,1,2}$

(ii) For S = 0

We take the remaining L values i.e.

L = 0, 2

For L = 0, S = 0 J = 0, term is ${}^1S_0$ Parity is even, as $\Sigma\ell$ for p^2 = even

For L = 2 S = 0 J = 2 term is ${}^1D_2$

- **The terms for various electrons configurtion are given as:**

Electonic configuration	Terms
s^1	${}^2s_{1/2}$
s^2, p^6, d^{10}, f^{14}	${}^1s_0$
p^1, p^5	${}^2p^0_{1/2,3/2}$
p^2, p^4	${}^1s_0, {}^1D_2, {}^3p_{0,1,2}$
p^3	${}^2p^0_{1/2,3/2}, {}^2D_{3/2,5/2}, {}^4s^0_{3/2}$
d^1, d^9	${}^2D_{3/2,5/2}$
d^2, d^8	${}^1S_0, {}^1D_2, {}^1G_4, {}^3P_{0,1,2}, {}^3F_{2,3,4}$

- **Order of terms and fine structure levels:**

The relative energies of the various terms and levels which arise from a given (equivalent) electron configuration may be deduced from a set of rules given by hund. These rules are:

(i) Of the terms arising from equivalent electron, those with largest multiplicity (2s+1) lie lowest.

(ii) Of the terms with given multiplicity and arising from equivalent electron, that with largest L, value lies lowest.

(iii) (a) In the multiplets formed from equivalent electron in a less than half-filled subshell, the level with lowest J, lies lowest (normal order).

(b) In the multiplets formed from equivalent electron in a more than half filled subshell, the level with highest J lies lowest (inverted order)

(c) Terms arising from half filled subshell show only very slight fine structure splitting.

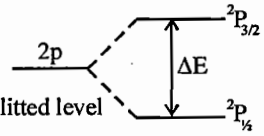
(d) The lowest terms arising from half filled subshell are the s-terms and are specially stable. These terms are ${}^2s_{1/2}$ for a half filled s-subshell, ${}^4s_{3/2}$ for a half-filled p-subshell, ${}^6s_{5/2}$ for a half filled d-subshell and ${}^8s_{7/2}$ for a half-filled f-subshell.

Hund was quite successful in predicting the lowest terms and levels of many atoms. However exceptions do occur:

Example:

Atom	Electronic configuration	Terms
${}_5B$	$1s^2, 2s^2, 2p^1$	${}^2P^0_{1/2}$ (ground), ${}^2P^0_{3/2}$
${}_6C$	$1s^2, 2s^2, 2p^2$	${}^1S_0, {}^1D_2, {}^3P_0$ (ground), ${}^3P_1, {}^3P_2$
${}_7N$	$1s^2, 2s^2, 2p^3$	${}^2P^0_{1/2}, {}^2P^0_{3/2}, {}^2D_{3/2}, {}^2D^0_{5/2}, {}^4S^0_{3/2}$ (ground)
${}_8O$	$1s^2, 2s^2 2p^4$	${}^1S_0, {}^1D_2, {}^3P_0, {}^3P_1, {}^3P_2$ (ground)
${}_9F$	$1s^2, 2s^2, 2p^5$	${}^2P^0_{3/2}, {}^2P^0_{1/2}$ (ground)
${}_{17}Cl$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^5$	${}^2P^0_{3/2}, {}^2P^0_{1/2}$ (ground)

SPIN-ORBIT INTERACTION



Splitted due to spin orbit interaction.

The term shift in cm^{-1}.

$$\Delta T = -\frac{\Delta E}{hc} = 5.84 \frac{Z^4}{n^3 \ell(\ell+1)} cm^{-1}$$

$$\Delta T \propto Z^4$$

Problem: The doublet splitting of the first excited state, ${}^2P_{3/2} \rightarrow {}^2P_{1/2}$ of He^+ is $5.84\ cm^{-1}$. Calculate the corresponiding spectrum for H and Li^{++}

Ans. $\left[0.365\ cm^{-1}, 29.6\ cm^{-1}\right]$

Solved Problems:

1. If the doublet splitting of the first excited state, $2\,{}^2P_{3/2} - 2\,{}^2P_{1/2}$, of He^+ is $5.84\ cm^{-1}$, calculate the corresponding seperation for H.

Soln. The doublet splitting (term difference) of a one-electron atomic state arising due to spin-orbit interaction is given by

$$\Delta T = \frac{R_\infty \alpha^2 Z^4}{n^3 \ell(\ell+1)}\ cm^{-1}$$

Where R_∞ is Rydberg constant for infinitely heavy nucleus, α is fine-structure constant and Z is atomic number

For a given state $(n, \ell$ constant$)$, we have

$$\Delta T \propto Z^4$$

Now, for He^+, $Z = 2$ and for H, Z = 1

$$\therefore \quad \frac{\Delta T_{He^+}}{\Delta T_H} = \frac{(2)^4}{(1)^4} = 16$$

Or, $\Delta T_H = \frac{1}{16}\Delta T_{He^+} = \frac{1}{16}\times 5.84\ cm^{-1} = 0.365\ cm^{-1}$

2. The doublet splitting of the first excited state $^2P_{3/2} - ^2P_{1/2}$ of H atom is 0.365 cm^{-1}. Calculate the corresponding separation for Li^{++}.

Soln. For Li^{++} and H, Z = 3 and 1 respectively.

$$\therefore \quad \frac{\Delta T_{Li^{++}}}{\Delta T_H} = \frac{(3)^4}{(1)^4} = 8$$

Or, $\Delta T_{Li^{++}} = 81\,\Delta T_H = 81\times\left(0.365\ cm^{-1}\right) = 29.6\ cm^{-1}$

3. Calculate the spin-orbit interacting splitting of a levl corresponding to n = 2 and l = 1 of hydrogen atom.

Soln. The spin-orbit interacting splitting of an energy level is given by

$$\Delta T = 5.84\frac{z^4}{n^3\ell(\ell+1)}\ cm^{-1}$$

Here $n = 2$, $\ell = 1$ and $Z = 1$ (for hydrogen atom)

$$\therefore \quad \Delta T = 5.84\left(\frac{1}{2^3\times 1\times 2}\right) = 0.365\ cm^{-1}$$

Spectra of Alkali elements:

- **Broad feature of Alkali Spectra:**

After H-atom, the simplest atoms to study with regard to their spectra are the 'Alkali atoms' Li, Na, K, Rb, Cs & Fr. The experimental study of their spectra was taken up by livening, Dewar Rydberg and Bergmann spectral lines in the emission spectrum of an alkali atom formed four series a principal series of bright and most presistant lines, a sharp series of fine lines a diffuse series a comparitively broader lines and fundamental (or Bergymann) series in the infra-red region

Taking clue from of the Balmer's formula for H.

$$\boxed{\nu_m^B = \nu_\infty^B - \frac{R}{n^2}}$$

Rydberg pointed out that the alkali series could be represented by similar formula such as

(i) Principal : $\nu_m^p = \nu_\infty^p - \frac{R}{(m+p)^2}$; $m = 2,3,4.....\infty$

(ii) Sharp : $\nu_m^s = \nu_\infty^s - \frac{R}{(m+s)^2}$; $m = 2,3,4.....\infty$

(iii) Diffuse : $\nu_m^D = \nu_\infty^D - \frac{R}{(m+d)^2}$; $m = 3,4,5.....\infty$

(iv) Fundamental : $\nu_m^f = \nu_m^f - \frac{R}{(m+f)^2}$; $m = 3,4,5.....\infty$

Where $\nu_\infty^{'s}$ are the wave number of convergence limits of the corresponding series and are called 'fixed terms'. In the other so clled running terms. p, s, d and f represent Rydberg corrections for the corresponding series.

Rydberg noticed the following relations among different series of the same atom. These are

(i) The sharp and diffuse series have a common convergence limit

$$\left[\nu_\infty^s = \nu_\infty^d\right]$$

(ii) The common convergence limit is equal to the first running term (with m = 2) of the principal series

$$\left[\nu_\infty^s = \nu_\infty^d = \frac{R}{(2+p)^2}\right]$$

(iii) The convergence limit of the principal series is equal to the running term (with m = 1) of the sharp series.

$$\left[\nu_\infty^p = \frac{R}{(1+s)^2}\right]$$

(iv) The convergence limit of the fundamental series is equal to the Ist running term (with m = 3) of the diffuse series).

$$\left[\nu_\infty^f = \frac{R}{(3+d)^2}\right]$$

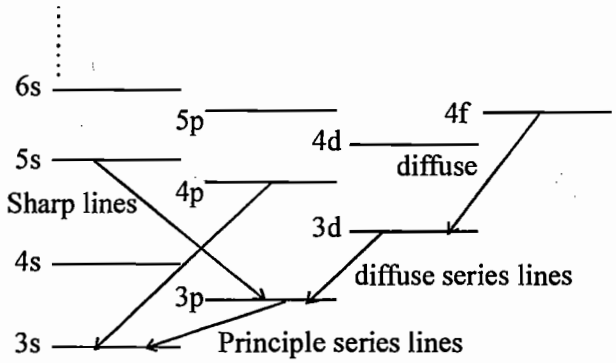
In view of these observations the above formula may be written in the following form:

(i) Principal : $\nu_m^p = \frac{R}{(1+s)^2} - \frac{R}{(m+p)^2}$; $m = 2,3,4....\infty$

(ii) Sharp : $\nu_m^s = \frac{R}{(2+p)^2} - \frac{R}{(m+s)^2}$; $m = 2,3,4.....\infty$

(iii) Diffuse : $\nu_m^d = \frac{R}{(2+p)^2} - \frac{R}{(m+d)^2}$; $m = 4,5.....\infty$

(iv) Fundamental : $\nu_m^f = \frac{R}{(3+d)^2} - \frac{1}{(m+1)^2}$; $m = 4,5,.....$



[Emission spectra of sodium]

ZEEMAN EFFECT

(Discovered by Zeeman in 1896)

Zeeman observed the effect of external magnetic field ($\left(\sim\frac{1}{10}\text{ Tesla}\right)$ on spectrum lines and he observed that the spectrum line is splitted into a number of components. The electric vector of some of the lines is parallel to the applied magnetic field (π-component) while the electric field vector of some of the lines is transverse to the external magnetic field and are called σ-components.

Types of Zeeman effect: In zeeman effect the energy levels are also splitted in external magnetic field, as a result of it the lines are splitted. It is of two types.

(i) **Normal Zeeman effect:** Normal zeeman effect happen in the energy levels in which s = 0 (i.e singlet) magnetic field is relatively strong. In Normal Zeeman effect the lines get splitted into smaller number of components i.e. 2 or 3 components.

(ii) **Anamalous Zeeman effect:** This happens in the energy levels in which $s \neq 0$ and magnetic field is weak. In anamalous zeeman effect the lines get splitted in large number of components (more than 3).

Explanation of Zeeman effect: Quantum theory was quite successful in explaning both kind of zeeman effects. Classial theory (given by Lorentz) was only able to explain normal zeeman effect.

Quantum theory of normal zeeman effect:

For normal zeeman effect s = 0, therefore the total A.M. of the atom is orbital and hence only orbital magnetic dipole moment (μ_2). This orbital magnetic moment of atom interact with the external magnetic field, as a result of it the energy of the level is changed and he level is splitted.

Due to the ineraction of μ_L with B, $\vec{\mu}_L$ or $\vec{L}$ precess around B (Lormor Precession).

The interaction energy

$$\upsilon = -\vec{\mu}_L.\vec{B}$$

$$= -\mu_L B\cos\theta$$

$$= -\left(\mu_L\cos\theta\right)B = -\mu_{L_z}B$$

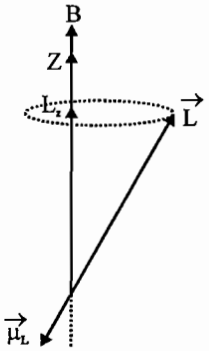
$$= -g_\ell\left(\frac{e}{2m}\right)\left|\vec{L}_z\right|B = -g_\ell\frac{e}{2m}M_L\hbar B$$

$$\upsilon = -g_\ell\frac{eh}{4\pi m}M_L B \qquad g_\ell = \text{orbital g factor} = 1$$

$$= \frac{eh}{4\pi M}M_L B$$

Interaction energy in terms of wave number shift

$$(\Delta T) = -\frac{(U \text{ or } \Delta E)}{hc} = \frac{eB}{4\pi mc}M_L\ cm^{-1}$$

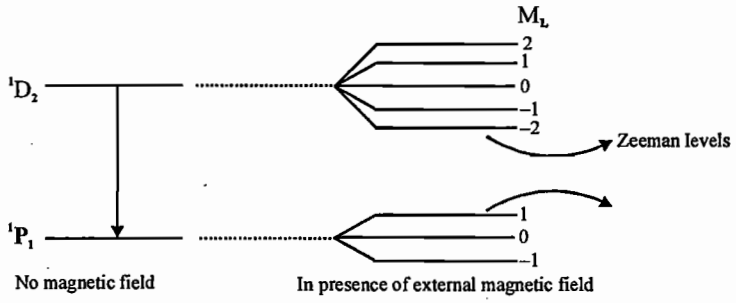


$\Delta T = M_L L' cm^{-1}$ $\quad L'$ = Lorentz unit $= \dfrac{eB}{4\pi mc}$ = constant for constant magnetic field.

For a given L,

$M_L = -L, -L+1, \ldots\ldots (L-1), L$

Ex. Let us consider the normal zeeman splitting of levels $^1D_2$ & $^1P_1$ and the five structure line $^1D_2 \rightarrow {}^1P_1$.



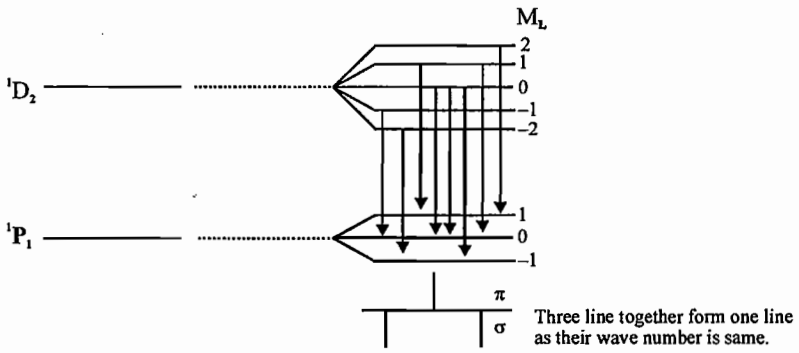
The separation between consecutive normal zeeman levels is same for both upper and lower levels (i.e. splitted $^1D_2$ and $^1P_1$ zeeman levels).

As the levels are splitted into number of components, therefore more number of spectrum lines will be observed. The selection rule for observed lines are

$$\boxed{\Delta M_L = 0, \pm 1}$$

$\Delta M_L = 0$ give π-components

$\Delta M_L = \pm 1, \sigma -$ components



- The seperation between consecutive levels in normal zeeman effect in terms of energy is:

$$\Delta E = \frac{eB}{4\pi m} hM_{L_2} - \frac{eB}{4\pi m} hm_{L_1} = \frac{eB}{4\pi m}\left(M_{L_2} - M_{L_1}\right)h$$

For consecutive levels.

$$M_{L_2} - M_{L_1} = 1$$

$$\Delta E = \frac{eB}{4\pi m} h$$

In terms of frequency.

$$\Delta E = h\Delta\upsilon = \frac{eB}{4\pi m} h \qquad \Rightarrow \qquad \boxed{\Delta\upsilon = \frac{eB}{4\pi m}}$$

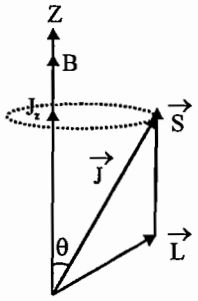
In terms of wavelength, as $\upsilon = c/\lambda \Rightarrow \quad \Delta\upsilon = \dfrac{-c}{\lambda^2}\Delta\lambda$

$\Rightarrow$ $\boxed{\Delta\lambda = \frac{\lambda L}{c}\frac{eB}{4\pi m}}$ By measuring $\Delta\lambda$.

We can found e/m.

Explanation of Anamalous zeeman effect
(Wave field zeeman effect):

Here $s \neq 0$, and field is weak, therefore the strength of coupling between $\vec{L}$ & $\vec{S}$ is good enough therefore the resultant angular momentum is $\vec{J}$. The resultant angular momentum $\vec{J}$ process around $\vec{B}$. The interaction energy in this case is



$$U = -\bar{\mu}_J.\bar{B} = -\mu_J \cos\theta B$$

$$U = -\mu_{J_z} B$$

$$U = -g_J \frac{e}{2m} m_J \hbar B$$

$$m_J = -J, -J+1, \ldots\ldots (J-1), J$$

Here g_j or $g = 1 + \frac{J(J+1) - L(L+1) - S(S+1)}{2J(J+1)}$ is known as Lande g factor and this gives the relative separation of the zeeman levels for the different term.

$$\mu_J = g\frac{eh}{4\pi mc}\sqrt{J(J+1)}$$

The energy of precession is given by.

$$\Delta E = \omega J_z = g\, M_J \frac{eh}{4\pi mc} B$$

or, $$-\Delta T = g\, M_J \frac{eB}{4\pi mc^2} = g\, M_J\, L' \qquad \because L' = \frac{eB}{4\pi mc^2} \text{ (Lorent unit)}$$

it show that each J level is split into (2J + 1) equispaced zeeman level corresponding to the possible values of M_J.

Selection rule for component :

$\Delta M_J = 0$ polarised with electric vector parallel to $\vec{B}$ π-component.

$= \pm 1$ polarised with electric vector perpendicular to $\vec{B}$ (σ-component)

"The sum of all the transition starting from any initial zeeman level is equal to the sum of the all transition starting from any other level having the same n & *l* values. The sum of all transition arriving at any zeeman level in equal to the sum of all transition arriving at any other level having the same n & l values".

Paschen-Back effect :

However the strength of the external field is increased the separation between zeeman component increases until they become greater than the separation between multiplet fine structure component. The anomalouszeeman pattern. Then changes over tolike a normal zeeman effet. This is known as Paschen Back effect.

When external field B is stronger than internal field then coupling between L and S partially broken and L and S independently process about external field. Here L_z and S_z are quantized component (along field dir^n)of L and S.

$$L_z = M_L\hbar \quad S_z = M_S\hbar$$

The sum these two interaction energies is the main energy shift ΔE inperturbed energy level and

$$\Delta E + \Delta E_L + \Delta E_S = (M_L + 2M_S)\frac{eh}{4\pi mc}B$$

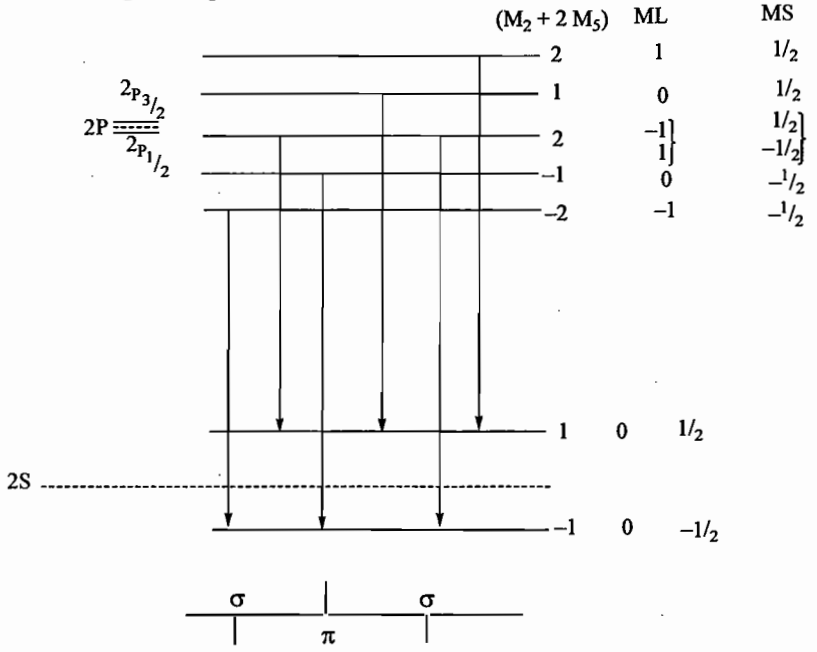
or, $\quad -\Delta T = (M_L + 2M_S)L' \text{ cm}^{-1}$

Let us consider the transition.

$2p \rightarrow 2s$ in strong field. This transition in responsible of D_1 and D_2 lives of sodium.

Term	**No. of strong field level (2L+1) (2S+1)**	M_L	M_S	**Shift in Lorentz unit** $(M_L + 2M_S)$
2p	6	1	$\frac{1}{2}, -\frac{1}{2}$	2, 0
(L = 1, S = 1/2)	0	$\frac{1}{2}, -\frac{1}{2}$	1, −1	
2S	−1	$\frac{1}{2}, -\frac{1}{2}$	0, −2	
(L = 0, S = 1/2)	2	0	$\frac{1}{2}, -\frac{1}{2}$	1, −1

The strong field splitting of the term 2P and 2S have been shown as.



In a strong field, the selection rules for transition are.

$\Delta M_L = 0$ (component polarised || to field)

$\Delta M_L = \pm 1$ (component polarised $\perp$ to field)

$\Delta M_S = 0$

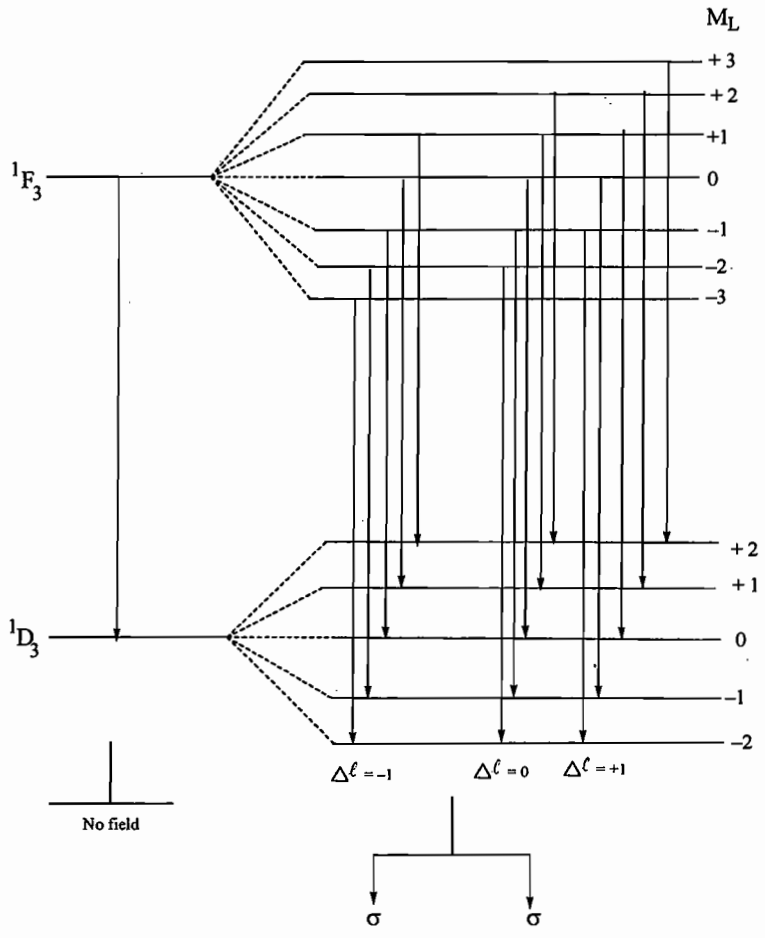
Spin -orbit correction :

The residual spin orbit coupling changes the relative energies of the component of different term, thus $-\Delta T\,(M_L + 2M_S)\,L' + a\,M_L\,M_S\ cm^{-1}$. As a result of this each of the two σ component of the normal triplet splits into narrow doublets triplets according as the orginial field free transition was doublet, tripletes etc. For intermediate field (comparable with internal field) complicated patterns are obtained.

Few example of zeeman effect :

(i) $^1F_3 — {}^1D_2$, it is a singlet-singlet transition and give rise to a normal zeeman triplet.

unperturbed level	No. of zeeman level (2L + 1)	M_L (+L – – L)	Shift in Lorentz unit M_L
$^1F_3$		+3, +2, +1	3L, 2L, L
	7	0	0
(L = 3, S = 0, J = 3)		– 3, – 2, – 1	– 3L, – 2L, – L
$^1D_2$		+ 2, + 1	2L, L
(L = 2, S = 0, J = 2)	5	0	0
		–2, – 1	– 2L, – L



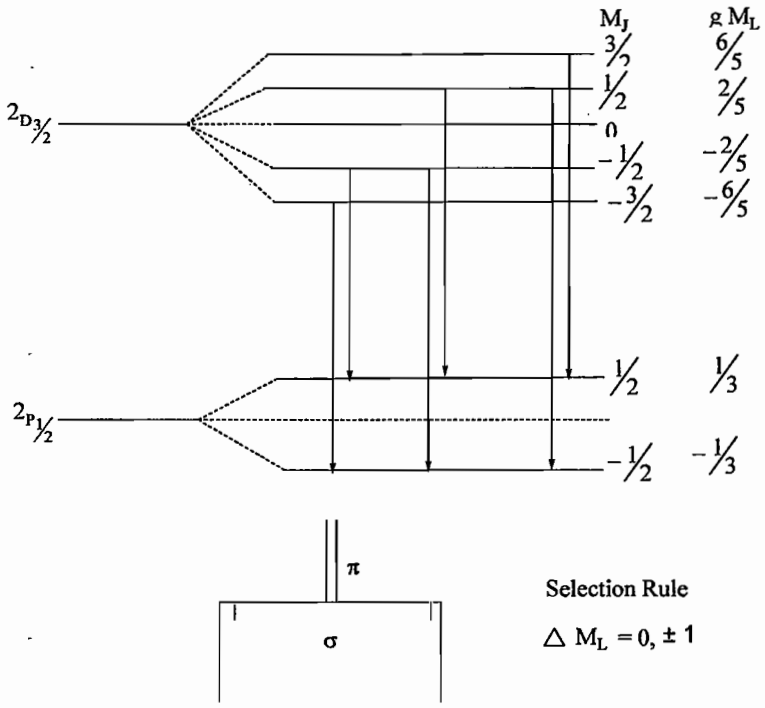
Selection Rule

$$\boxed{\Delta M_L = 0,\ \pm 1}$$

(ii) $^2D_{3/2} - {}^2P_{1/2}$, It is a doublet-doublet transition so that the zeeman pattern be anomalous.

Here, $g = 1 + \dfrac{J(J+1) - L(L+1) - S(S+1)}{2J(J+1)}$

Term	No. of zeeman (2J + 1)	g	M_J (+J .....J)	Shift in L' unit g M_J
$^2P_{1/2}$ (L=1, S = 1/2, J =1/2)	2	2/3	1/2 −1/2	1/3, −1/3
$^2D_{3/2}$ (L=2, S=1/2, J=3/2)	4	4/5	3/2 1/2 −1/2 −3/2.	6/5, 2/5, –2/5, – 6/5



Problem: Show the splitting of sodium D lines i.e. D_1 $\left(^2P_{1/2} - ^2S_{1/2}\right)$ & D_2 lines $\left(^2P_{3/2} - ^2S_{1/2}\right)$ in weak mag. field and find the number of zeeman components

Ans. [4 and 6]

STARK EFFECT

(Discovered by J. Stark in 1913).

Splitting of spectrum lines in presence external electric field (F) ~ 10^5 volt/cm.
There is no first order stark effect in ground state of H-atom.

As H' = work done in E.F. by electron

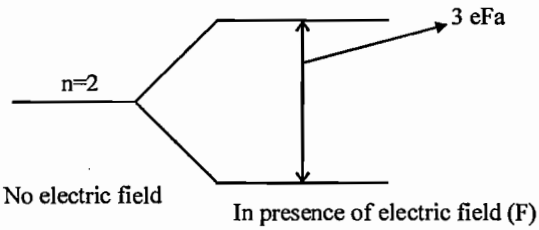
$$= -e\vec{F}.\vec{r} = -eFr\cos\theta = \text{Perturbed Hamiltonian}$$

And E' = interaction energy = $\int_{r=0}^{\infty}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} \psi_{100}^{*} H' \psi_{100} \underbrace{d\tau}_{r^2\sin\theta dr d\theta d\phi}$

$$= 0$$

$$\psi_{100} = \frac{1}{\sqrt{\pi a_0}} e^{-r/a_0}$$

- For H-atom for I[st] excited state n = 2.



- **Stark effect partially lift the degeneracy**
- **It is of two types**
  (a) Weak field stark effect.
  (b) Strong field stark effect.

Hyperfine structure of spectral lines (hfs)

Many fine structure components of spectral lines, when examined under instruments of highest possible resolution, are further splitted into components with seperations of the order 1 cm^{-1}, which is very smaller. This is called "hyper fine structure and is explained by considering the following two factors of atomic nucleus. These are

(i) **Isotope effect:** (Different isotopes of an element has different mass and hence different Rydberg constant and hence energy levels.)

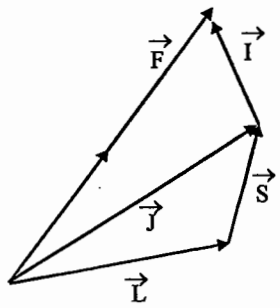
(ii) **Nuclear spin (I):** Bi(Bistmuth) has only one isotope in nature but shows six hyperfine components, thus another thing i.e. nuclear spin is also invoved in hyperfine structure.

- **Vector model of atom for hfs:**

Let us now construct the vector model with nuclear spin taken into account. The total angular momentum $(\vec{F})$ of the whole atom is the sum of three angular momenta. The electron orbital angular momentum $(\vec{L})$, the electron spin angular momentum $(\vec{S})$ and the nuclear spin angular momentum $(\vec{I})$.

$\therefore \quad \vec{F} = \vec{L} + \vec{S} + \vec{I} = \vec{J} + \vec{I}$

And Its magnitude $|\vec{F}| = \hbar\sqrt{F(F+1)}$, $F = |J-I|, \ldots\ldots\ldots (J+I)$

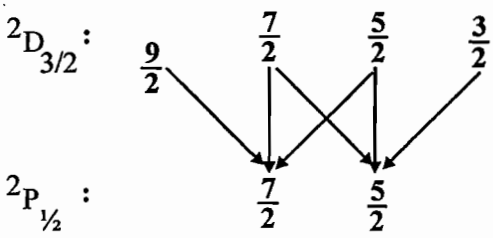


The selection rule on F are similar to that of J.

i.e. $\Delta F = 0, \pm 1$

But F = 0 $\longleftarrow\!\!\!

Hence the allowed transitions from the levels of one state to those of the other are;



In all there are six transitions. Hence, the number of expected hfs components is 6.

2. The nuclear spin of bismuth atoms is 9/2. Using this, find the number of levels in which the term $^2D_{5/2}$ of bismuth will split due to $\vec{I}-\vec{J}$ interaction. If the separation of the $^2_2D_{5/2}$ and $^2_3D_{5/2}$ levels is 30 cm^{-1}, calculate the separations of the rest of the adjacent levels.

($^2_2D_{5/2}$: F value)

Soln. For bismuth atom, we have

$$I=\frac{9}{2}$$

and for its state $^2D_{5/2}$, we have

$$J=\frac{5}{2}$$

The allowed values of the hfs quantum number are

$$F=J+I, J+I-1, \ldots\ldots\ldots\ldots |J-I|$$

$$=7,6,5,4,3,2.$$

So that there are six hfs levels, which are designated as*

$$^2_7D_{5/2}, ^2_6D_{5/2}, ^2_5D_{5/2}, ^2_3D_{5/2}, ^2_2D_{5/2}$$

The separation between two successive levels F and F+1 is given by Lande's interval rule, that is,

$$\Delta E' = A'(F+1)$$

Therefore, as the separation between $^2_2D_{5/2}$ and $^2_3D_{5/2}$ level is 30 cm^{-1}, we have

$$30\ cm^{-1} = A'(3)$$

Or, $$A' = 10\ cm^{-1}$$

Hence, the separation between other levels are:

$$^2_3D_{5/2} - ^2_4D_{5/2} = 10\times 4 = 40\ cm^{-1}$$

$$^2_4D_{5/2} - ^2_6D_{5/2} = 10\times 6 = 60\ cm^{-1}$$

$$^2_5D_{5/2} - ^2_6D_{5/2} = 10\times 6 = 60\ cm^{-1}$$

$$^2_6D_{5/2} - ^2_7D_{5/2} = 10\times 7 = 70\ cm^{-1}$$

These separations have been shown in Fig.

$^2D_{5/2}$ — 7 — 70 cm^{-1}

$^2D_{5/2}$ — 6 — 60 cm^{-1}

$^2D_{5/2}$ — 5 — 50 cm^{-1}

$^2D_{5/2}$ — 4 — 40 cm^{-1}

$^2D_{5/2}$ — 3 — 30 cm^{-1}

$^2D_{5/2}$ — 2 — 20 cm^{-1}

Fig.

X-RAYS

- **X-rays:** X-rays was discovered by Rontgen in 1896. Rongten got nobel prize for the discovery of X-rays in 1901. He was the first physicist to get the noble prize for discovery of X-rays.

$$E = h\nu$$

$$= h\frac{c}{\lambda}$$

X-rays are high energy photons: Whose wavelength lies between 1Å to 100Å.

- **Types of X-rays:**

X-rays can be divided on the basis of energy and on the basis of spectrum shown.

(i) On the basis of energy: On the basis of energy X-rays are of two types:

(a) Soft X-rays: These are the X-rays of low energy. The wavelength of soft X-rays lies from 4Å→100Å.

(b) Hard X-rays: These are the X-rays of high energy. The wavelength of hard X-rays lies from 1Å→ 4Å.

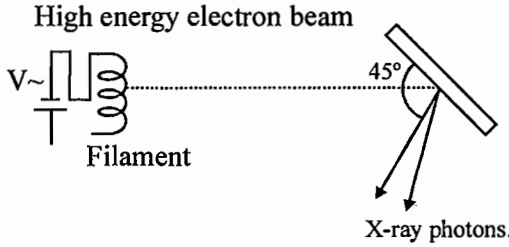
(ii) On the basis of spectrum shown: On the basis of spectrum shown X-rays are divided into two parts:

(a) Continuous X-rays: Contains all possible wavelength between 1Å → 100Å and λ depends on V (applied voltage)

(b) Characteristic X-rays: Contains only certain wavelength which are the characteristic of the target material i.e. λ depends on z (atomic number).

- **Production of X-rays:**

X-rays are produced, when a high energy electron beam strikes to a heavy target [such as M0, W(tungsten)]. The target is placed at an angle of 45° with the direction of incident electron beam. The melting point of target should be high, so that it doesn't get melt by the high energy electrons..

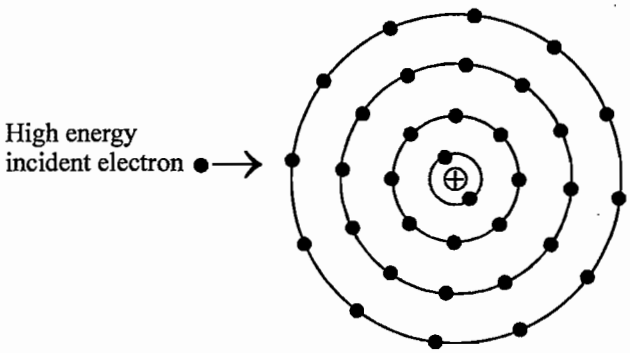


[Production of X-rays by modern cooledge tube]

The production of X-rays is based upon inverse photo-electric effect.
Only 1% electron are responsible for the production of X-rays

- **Mechanism of production of continuous X-rays:**

When electron of high energy are incident on a heavy material, then electron gets accelerated or deaccelerated by the nucleus and other electrons of the atoms of the material.



The electromagnetic theory says that when a charge particle gets accelerated or deaccelerated, it radiates energy. The energy radiated by the electron in such procss comes out as continuous X-rays. (This is called Bremsstrahlung)

Thus, the max. energy lost by electron = Max. energy of X-ray photon.

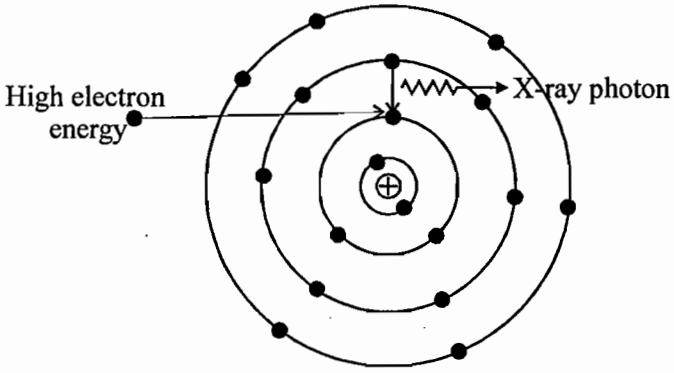
$$\Rightarrow \quad eV = \frac{hc}{\lambda_{min}}$$

$$\Rightarrow \quad \boxed{\lambda_{min} = \frac{hc}{eV} = \frac{12375}{V}\text{Å}} \qquad \text{... (1)}$$

Equation (1) is called duane-Hunt law. This equation gives the minimum wavelength of emitted X-rays photon. For X-rays V should be in kilovolt.

Mechanism of production of characteristic X-rays:

When high energy incident electron strikes to any of the atomic electron and electron is displaced from its orbit. So, the electron from outer orbit jump to the lower orbit just to fill the vacancy. Thus a photon of energy equal to the energy difference between two energy levels comes out. This photon is in the form of of characteristic X-rays. Thus the energy of the characteristic X-ray photon is:



$$\frac{hc}{\lambda} = E_i - E_f$$

$$\Rightarrow \quad \frac{hc}{\lambda} = -\frac{R(z-\sigma)^2 hc}{n_i^2} - \left(-\frac{Rhc(z-\sigma)^2}{n_f^2}\right)$$

$$\Rightarrow \quad \boxed{\frac{1}{\lambda} = R(z-\sigma)^2\left[\frac{1}{n_f^2} - \frac{1}{n_i^2}\right]}$$

Here z = atomic number of the target and σ = screening constant
Thus here we also get a series of X-ray lines.

- **k-series characteristic X-rays:**

If $n_f = 1$ and $n_i = 2,3,4.....\infty$. We get k-series lines. For k-series lines $\sigma = 1$.

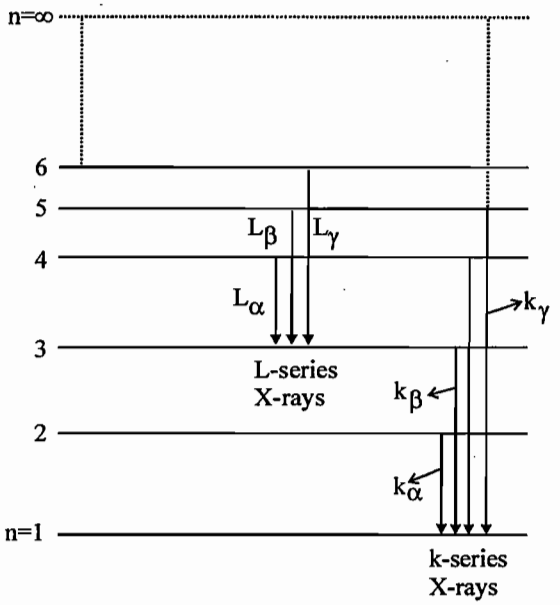
$\therefore$ Wavelength of k_α, k_β, k_r ..... lines are

$$\frac{1}{\lambda_{k_\alpha}} = R(z-1)^2\left[\frac{1}{1^2} - \frac{1}{2^2}\right]$$

$$\frac{1}{\lambda_{k_\beta}} = R(z-1)^2\left[\frac{1}{1^2} - \frac{1}{3^2}\right]$$

$$\frac{1}{\lambda_{k_\gamma}} = R(z-1)^2\left[\frac{1}{1^2} - \frac{1}{4^2}\right]$$

.....



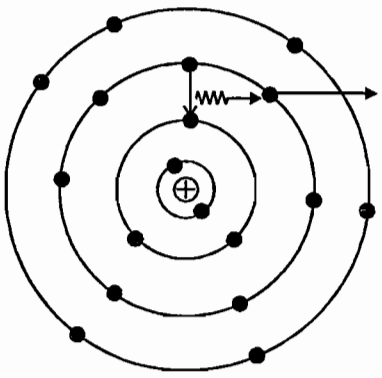
- **For L-series characteristic X-rays**

$$\Rightarrow \quad \frac{1}{\lambda_{L_\alpha}} = R(z-7.4)^2\left[\frac{1}{2^2} - \frac{1}{3^2}\right]$$

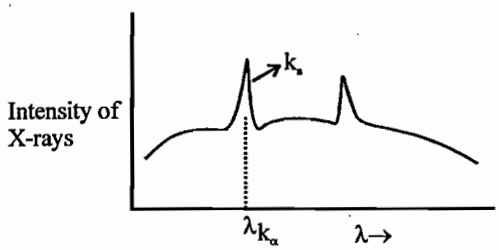
Similarly, for L_β, L_r, L_δ lines

- **Auger effect or inner photoelectric effect:**

Augur founded that the x-ray photon which is created by the transition of an electron in inner shells may be absorbed by any atomic electron and then the electron comes out rather than X-ray photon. Thus the intensity of X-ray photons decreases. This is called Auger effect.



- **Spectra of X-rays:**



Q. Calculate minimum value of potential must be applied to produce X-ray photon of $\lambda = 0.1\mathring{A}$

$$V_0 = \frac{12375}{\lambda_{\min}} = \frac{123750}{1} = 1.25\times10^5 v$$

Q. If the k_α radiation of $M_0\,(z=42)$ has a wavelength of 0.71 Å. Calculate the λ corresponding to $Cu(z=29)$

$$\frac{\lambda_{Cu}}{\lambda_{M_0}} = \frac{(Z_{m_0}-1)^2}{(Z_{Cu}-1)^2} = \frac{(41)^2}{(28)^2} \qquad \lambda_{Cu} = 1.52\mathring{A}$$

Q. How much energy goes to quantum state emitted when an L-electron (n = 2 state) drops to k-state (n = 1 state) in Cu (z= 29). Given
R = 109737 cm^{-1}.
1 cm^{-1} = 1.239×10^{-4} eV/cm^{-1}.

Soln. By Moselay law, X-ray wavelength emitted

$$\frac{1}{\lambda} = R(z-1)^2\left(\frac{1}{1^2}-\frac{1}{2^2}\right) = \frac{3}{4}R(z-1)^2 \quad \text{correspond to } k_\alpha \text{ line}(\sigma=1)$$

$$\frac{1}{\lambda} = \frac{3}{4}(109737\ cm^{-1})(28)^2 = 6.4525\times10^7\ cm^{-1}$$

Corresponding en. emitted is $= 6.4525\times10^7\ cm^{-1}\times1.239\times10^{-4}\ ev/cm^{-1}$

$$= 7994.6\ eV$$

Q. If the series limit of Balmer series for H is 346.6 cm. Calculate the atomic number of element which give X-ray wavelength down to 0.1 nm. (i.e. k-series).

Soln. Balmer series for H is $\frac{1}{\lambda} = R\left(\frac{1}{2^2}-\frac{1}{n_2^2}\right)$

If series limit $(n_2=\infty)$ is $\lambda_\infty = 346.\lambda\ cm$

$$\frac{1}{\lambda_\infty} = R\left(\frac{1}{2^2}-\frac{1}{\infty}\right) = \frac{R}{4} \qquad R = \frac{4}{\lambda_\infty} = \frac{4}{346.6}\ nm$$

By Moselay law:

$$\frac{1}{\lambda} = R(z-1)^2\left(\frac{1}{1^2}-\frac{1}{n^2}\right)$$

For mini λ of this series occur when $m=\infty$

$$\frac{1}{\lambda} = R(z-1)^2$$

$$(z-1)^2 = \frac{346.6}{4}\alpha_{01\,bn} = 911.5$$

$$z-1=30.2$$

$$z=31.2,\quad z=31$$

Q. If the K, L, M en. levels of platinum involved in the emission of k-series of X-rays of this element are 78,000, 12000, 3000 eV respectively. Calculate the λ of k_α & k_β lines.

k_α line observed when electron drop
L-shell to k-shell

$$h\nu=\frac{hc}{\lambda_{k_\alpha}}=E_1-E_2=78000-12000=66000\,eV=66000\left(1.6\times10^{-19}\right)J$$

$$\Rightarrow \text{for } k_a \qquad \frac{1}{\lambda_{k_\alpha}}=\frac{6600\times\left(1.6\times10^{-19}\right)J}{\left(6.6\times10^{-34}J-s\right)\left(3\times10^{8}\,m/s\right)} \qquad \lambda_{k_\alpha}=0.189\times10^{-10}m$$

$$\Rightarrow \text{for } k_\beta \qquad h\nu_{k_\beta}=78000-3000=75000\,eV$$

THE BREADTH OF SPECTRAL LINES

The intensity distribution of a typical spectral line may be expressed by an intensity (I) versus wave number (ν) cm^{-1} curve as shown in fig.1. below:

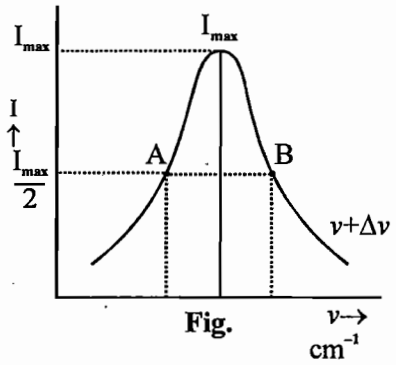
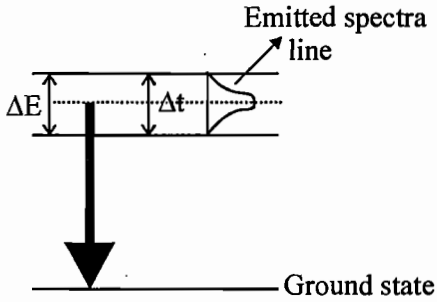


Fig.

The breadth of a spectral line is defined as the seperation in cm^{-1}, between two points A and B whose intensities are half that of maximum intensity (FWHM). The known causes of spectral-line breadth are the following:
(i) Natural breadth.
(ii) Doppler effect.
(iii) External effects: Collision damping, pressure broadering and stark effect.

Natural Breadth:



If ΔE is the energyy breadth from which the electron jump and spectrum line is emitted and let τ is the mean lift time of the this state, then

$\boxed{\Delta E.\Delta t \sim \hbar}$ (Heisenberg uncertainity principle)

gives

$$(h\Delta\nu)\tau \sim \frac{h}{2\pi} \qquad \begin{pmatrix} \text{As } E = h\nu \\ \Delta E = h\Delta\nu \end{pmatrix}$$

$$\Rightarrow \quad \boxed{\Delta\nu = \frac{1}{2\pi\tau}}$$

$$\Delta\nu = \frac{1}{2\pi \times 10^{-8}\,\text{sec}} \sim 10^7\ \text{sec}^{-1} \qquad \ldots (1)$$

In terms of wavelength (λ)

$$\nu = \frac{c}{\lambda} \quad \Rightarrow \quad \Delta\nu = -\frac{c}{\lambda^2}\Delta\lambda \qquad \ldots (2)$$

Putting (2) in (1), we have

$$\boxed{\frac{c}{\lambda^2}\Delta\lambda = 10^7}$$

$$\Delta\lambda = \frac{\lambda^2}{c} \times 10^7$$

For visible light $\lambda \sim 6000\mathring{A} = 6\times10^{-9}\,m$ & $c = 3\times10^8\ m/\text{sec}$

$\therefore \quad \Delta\lambda \sim 10^{-14}\,m \qquad \Delta\lambda \sim 10^{-4}\,\mathring{A}$

Which is very small.

Doppler effect:

By doppler effect if the emitted atom is in rapid random motion, the actual frequency ν_0 seems to be change to the observer. If the apparent frequency is v and v is the velocity of the source or atom, then motion of source observer.

$$\nu = \nu_0\left(1 + \frac{V}{c}\right)$$

$$\Rightarrow \quad \nu - \nu_0 = \pm\frac{\nu_0 V}{c} \qquad \ldots (1)$$

Using maxwellian distribution law, we get the relative intensity

$$I(\nu) = const.\exp\left[-\frac{\mu V^2}{2RT}\right] \qquad \ldots (2)$$

$(\mu = \text{atomic wave}))$

Or, $\quad i(\nu) = const.\exp\left[-\frac{\mu c^2(\nu-\nu_0)^2}{2RT\nu_0^2}\right] \qquad \ldots (2)$ (Using (1)

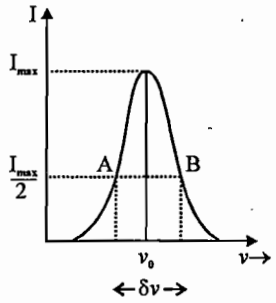
$I|_{\max} = const.\,[\text{at } \nu = \nu_0]$

The intensity is half of max. intensity at point A and B, where

$$\exp\left[-\frac{\mu c^2(\nu-\nu_0)^2}{2RT\nu_0^2}\right] = \frac{1}{2}$$

$$\Rightarrow \quad v - v_0 = \pm \frac{v_0}{c}\sqrt{\frac{2RT}{\mu}\log_e^2}$$

The line breadth $\delta v = 2(v - v_0) = 1.67\frac{v_0}{c}\sqrt{\frac{2RT}{\mu}}$



As $\log_e 2 = 0.693$

Also $\frac{\delta v}{v_0} = \frac{\delta \lambda}{\lambda_0}$

$$\Rightarrow \quad \boxed{\delta\lambda = 1.67\frac{\lambda_0}{c}\sqrt{\frac{2RT}{\mu}}}$$

Where λ = line breadth in terms of wavelength.

Problem: Calculate the doppler half-intensity breadht of sodium D-lines at 5893Å corresponding to a temperature of 500k. R = 8.31 Joule/mole-k $c = 3\times10^8\ m/s$ atomic wt. f $Na = 22.99\ gm/mole$.

Soln. $\delta\lambda = 1.67\frac{\lambda_0}{c}\sqrt{\frac{2RT}{\mu}}$

$$= 1.67\frac{\left(5893\times10^{-10}m\right)}{\left(3\times10^8 m/\sec\right)}\sqrt{\frac{2\times8.31\times500^\circ k(\text{Joule/mole }^\circ\text{k})}{22.99\times10^{-3}\ kg/mole}}$$

$\delta\lambda = 0.02\mathring{A}$.

Problem: Estimate the fractinal width of spectrum line of 5000Å wavelength emitted from a level of a life time of 10^{-8} sec

Ans. **[1.33×10^{-4} Å]**

Problem: A spectroscopic examination of the light from a certain star shows that the apparent wavelength of a certain line is 5001Å, whereas the observer wavelength of the same line is produced by a terrestrial source is 5000Å. In what direction and with what speed of the star is moving relative to the earth.

Ans. **[6×104 m/sec, away]**

MOLECULAR SPECTROSCOPY

Molecular spectra:

The emission and absorption spectra of a molecule arise from transition between allowed energy states, ground and excited states. The molecular spectra can be divided into 3 spectral ranges corresponding to different type of transistions between molecular energy states.

(i) **Electronic spectra:**

These spectra are observed, both in emission and absorption in visible and UV regions. The electronic spectra are observed for the heteronuclear as well as for homonuclear diatomic molecules i.e. HCl, HBr, H_2, N_2, O_2 etc. In it we observe bands. (λ lies in range $10^{-2}\ \mu - 10^{0}\ \mu$), E~10 eV. Permanent dipole moment is not necessary for showing electronic spectra.

(ii) **Vibrational-rotational spectra:($E \sim 10^{-1}$ eV)**

These spectra are observed in absorption in the near I-R region. (λ lies in the range $1\mu - 10^{2}\ \mu$). The vibrational rotational spectra are observed only forthe heteronuclear molecules. The homonuclear molecules like $(H_2, O_2, N_2$ etc.) do not produce vibrational-rotational bands as they do not have permanent dipole moment. In this spectra we observe bands.

(iii) **Pure rotational spectra:($E \sim 10^{-3}$ eV)**

These spectra are observed in absorption in the far infared region. (λ lies in the range $10^{2}\ \mu - 10^{3}\ \mu$ i.e. $10^{6}\ \text{Å} - 10^{7}\ \text{Å}$) or in the microwave ($\lambda$ lies in the range $10^{3}\ \mu - 10^{4}\ \mu$) region. Like vibrational rotational spectra, the pure rotational spectra are observed only for the heteronuclear diatomic molecules. In this spectra we obtain lines. Permanent dipole moment is necessary for a molecule to show this spectra.

PURE ROTATIONAL SPECTRA (FOR I-R REGION)

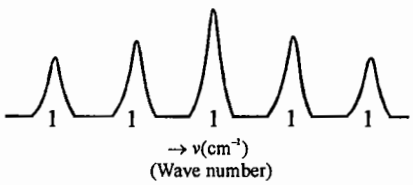
- **Salient features of Pure rotational spectra:**

Pure rotational molecular spectra arise from transitions between rotational energy states and are observed in the I-R $(\lambda \simeq 10^{2}\ \mu - 10^{3}\ \mu)$ or microwave $(\lambda \simeq 10^{3}\ \mu - 10^{4}\ \mu)$ region of the electromagnetic spectrum. Only molecule that have permament electric dipole moments can absorb or emit electromagnetic radiation in such transitions. This mean that homonuclear diatomic molecules such as O=C=O and spherical top polyatomic molecules such as CH_4 do not exhibit rotational spectra.

In practise, this spectra are observed in absorption for heteronuclear diatomic molecules such as HF, HCl, HBr, CO etc. It consists of a simple series of absorption maxima whicha are very nearly equidistant on a wave no. scale.

- A measurement of frequency of these maxima leads to a determination of moment of inertia and internuclear distance of the molecules

(Internuclear separation is fixed):

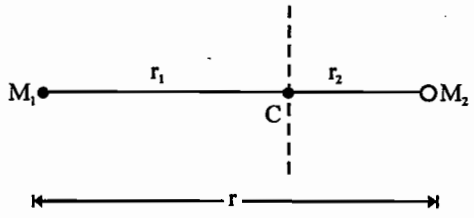


Explanation of pure rotational spectra:

The molecule as a rigid rotator:

The simplest example of this rotating diatomic molecule is that of a rigid rotator that is the internuclear separation is fixed at the equilibrium value.

Let us consider two atoms of masses m_1 and m_2 which are chemically bounded to form a diatomic molecule. Let 'r' be the distance between the two atoms and r_1, r_2 be the distance of the atoms from the molecular centre of mass M_1 and M_2 respectively.



The moment of inertia of this system about the axis of rotation, perpendicular to internuclear axis and passing through the centre of the mass i.e. given by

M.I. $\boxed{I = M_1 r_1^2 + M_2 r_2^2}$ ... (1)

And $r = r_1 + r_2$

by the principle of moment

$$\boxed{M_1 r_1 = M_2 r_2} \quad \text{... (2)}$$

Find r_1 and r_2 and put in (1)

$$r_1 = \frac{M_2 r_2}{M_1} \quad \Rightarrow \quad \frac{M_2}{M_1} = (r - r_1) \qquad (\text{as } r = r_1 + r_2)$$

$$r_1 = \frac{M_2 r}{M} - \frac{M_2 r_1}{M_1}$$

$$r_1 \frac{(M_1 + M_2)}{M_1} = \frac{M_2 r}{M_1}$$

$$r_1 = \frac{M_2 r}{(M_1 + M_2)}$$

And similarly $r_2 = \frac{M_1 r}{(M_1 + M_2)}$

From (1) $$I = M_1 \left(\frac{M_2 r}{M_1 + M_2}\right)^2 + M_2 \left(\frac{M_1 r}{M_1 + M_2}\right)^2 = \frac{M_1 M_2}{M_1 + M_2} r^2$$

$$\Rightarrow \quad \boxed{I = \mu r^2} \quad \text{.... (3)}$$

Where $\mu = \frac{M_1 M_2}{M_1 + M_2}$. $M_H = 1\ amu$ $M_{a35} = 35\ amu$

= reduce mass

Solving the Schrodinger equation for rigid rotator we get, $E = \frac{\hat{L}^2}{2I}$

$$\Rightarrow \quad \boxed{E \text{ or } E_J = \frac{J(J+1)\hbar^2}{2I}} \qquad \ldots (4)$$

Where J is the rotatinal Q.No. which can take the integral value $J = 0, 1, 2, 3.....$

Thus the rigid rotator have a discrete set of energy levels.

From classical mechanics, we have

$$E = \frac{1}{2} I\omega^2 \qquad \& \; L = I\omega \qquad \ldots (5)$$

So, that

$$L = \sqrt{2EI}$$

Thus the angular momentum (L) ofthe system in the quantum state (J) is given by

As $L = \sqrt{2EI}$

$$= \sqrt{\frac{2Ih^2}{8\pi^2} J(J+1)}$$

$$L = \frac{h}{2\pi}\sqrt{J(J+1)} = \hbar\sqrt{J(J+1)} \qquad \ldots (6)$$

Now, rotational angular frequency.

$$\omega = \frac{L}{I} = \frac{h}{2\pi I}\sqrt{J(J+1)} \qquad \ldots (7)$$

$\omega = 2\pi v_{rot}$

v_{rot} = Rotational frequency= $\frac{\omega}{2\pi}$

$$v_{rot} = \frac{h}{2\pi^2 .2I}\sqrt{J(J+1)} = \frac{h}{4\pi^2 I}\sqrt{J(J+1)}$$

In terms of wave number the energ can be written as, from equation (4).

$$F(J) = \frac{E}{hc} = \frac{h}{8\pi^2 Ic} J(J+1)\, cm^{-1}$$

$$\boxed{F(J) = BJ(J+1)} \qquad \ldots (9)$$

B = rotational constant.

Where $\boxed{B = \frac{h}{8\pi^2 IC}}$ ...(10)

Substituting $J = 0, 1, 2, 3.....$we get

$F(J) = 0, 2B, 6B, 12B, 20B$

Thus we have a series of discrete rotational energy levels. Whose spacing increasing with increasing J. When a transition takes place between an upper level J, and a lower level J". The wave number of emitted or absorved radiation would be given by

$$v = F(J') - F(J'')$$

$$= BJ'(J'+1) - BJ''(J''+1) \qquad \ldots (11)$$

A study of matrix elements of the dipole moment shows that the rotational transition can occur only such that J changes by unity. So that the selection rule is

$$\boxed{\Delta J = \pm 1}$$

$$J' - J'' = \pm 1$$

$\Rightarrow$ $J' - J'' = 1$ & $J' - J'' = -1$

Or $J'' = J' - 1$ & $J' = J'' + 1$

From (11) $v = B(J''+1)(J''+2) - BJ''(J''+1)$

$= 2B(J+1)$

Where J'' is the lower rotational state for simplicity we may with J for J'' thus

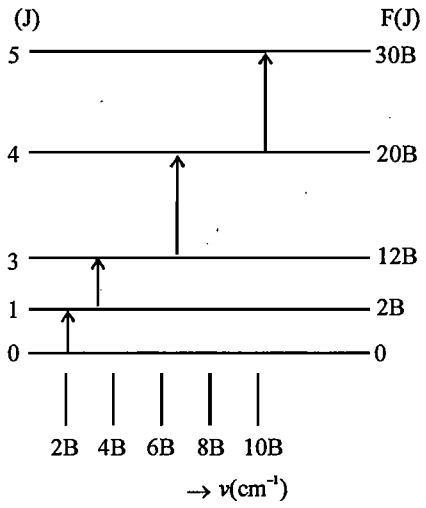
$$v = 2B(J+1)$$

$$J = 0, 1, 2.....$$

Substituting $J = 0, 1, 2$

$$v = 2B, 4B, 6B.....$$

Thus the absorption spectrum of a rigid rotation is expected to consist of a series of equidistant lines with constant separation (2B).



Seperation between consecutive lines = 2B

- $\frac{N_1}{N_0} \propto (2J+1)e^{-\Delta E/kT}$

  Where $(2J+1) \Rightarrow$ Degeneracy

  $\Delta E = E_{J+1} - E_J = 2B(J+1)hc$

- For non rigid rotator
  $F(J) = B\,J(J+1) - DJ^2(J+1)^2$
  D = Centrifugal distortionterm D<<B.

Problems:

1. The moment of inertia of the CO molecule is $1.46 \times 10^{-46}\ kg\ m^2$. Calculate the energy in eV and the angular velocity in the lowest rotational energy level of the CO molecule.

Soln. The quantum-mechanical energy of a rotating diatomic molecule is given by

$$E_J = \frac{h^2}{8\pi^2} J(J+1)$$

Where I is the moment of inertia of the molecule about the axis of rotation. The lowest rotational energy level corresponds to J = 1

$$\therefore \qquad E_1 = \frac{h^2}{8\pi^2 I} = \frac{h^2}{4\pi^2 I}$$

Substituting the value of h in M.K.S. units and the given value of I, we have

$$E_{J=1} = \frac{\left(6.62\times10^{-34}\,J-\sec\right)^2}{4\times(3.14)^2\times\left(1.46\times10^{-46}\ kg.m^2\right)}$$

$$= \frac{6.62\times10^{-34}\times6.62\times10^{-34}}{4\times3.14\times1.46\times10^{-46}\times3.14}$$

$$= 7.61\times10^{-23}\,J$$

But 1 eV = $1.6\times10^{-19}\ J$

$$\therefore \qquad E_{J=1} = \frac{7.61\times10^{-23}}{1.6\times10^{-19}}$$

$$= 4.75\times10^{-4}\ eV$$

The angular velocity of the (0 when J = 1)

$$\omega = \sqrt{\frac{2E}{I}} \qquad \left(\because E = \frac{1}{2}I\omega^2\right)$$

$$= \sqrt{\frac{2\times7.61\times10^{-23}}{1.46\times10^{-26}}}$$

$$= 10.2\times10^{11} \text{ rad/sec}$$

2. The $J=0\rightarrow J=1$ absorption line in CO occurs at a frequency of 1.153×10^{11} cycles/sec. Calculate the moment of inertia and internuclear separation of CO.

$\left(h = 6.62\times10^{-27}\ erg-\sec,\ N_A = 6.023\times10^{23}\right)$

Soln. The rotational energy of a diatomic molecule is given by

$$E = \frac{h^2}{8\pi^2 I}J(J+1)$$

The energy separation between J = 0 and J = 1 levels is:

$$\Delta E = E_{J=1} - E_{J=0} = \frac{h^2}{4\pi^2 I}$$

The frequency $\bar{\nu}$ absorbed in transition J = 0 → J = 1 is:

$$\bar{\nu} = \frac{\Delta E}{h} = \frac{h}{4\pi^2 I}$$

$$I = \frac{h}{4\pi^2\bar{\nu}} = \frac{6.62\times10^{-27}\ erg-\sec}{4\times(3.14)^2\times\left(1.153\times10^{11}\sec^{-1}\right)}$$

$$= 1.46\times10^{-39}\ gm-cm^2$$

The reduced mass of the CO molecule is given by

$$\mu_{OH} = \frac{M_C M_O}{M_C + M_O}$$

$$= \frac{(12\times16)/(6.023\times10^{33})^2}{(12+16)/(6.023\times10^{23})}$$

$$= \frac{12\times16}{28\times(6.023\times10^{23})} = 1.14\times10^{-23}\,g$$

$\therefore$ The internuclear separation (bond length) r is:

$$r = \sqrt{\frac{I}{\mu}} \qquad (\because\ I = \mu r^2)$$

$$= \sqrt{\frac{1.46\times10^{-39}\ gm-cm^2}{1.14\times10^{-23}\ gm}}$$

$$= 1.13\times10^{-8}\ cm = 1.13\ \mathring{A}$$

3. The OH^- radical has a moment of inertia of $1.48\times10^{-40}\ gm-cm^2$. Calculate its internuclear distance. Also calculate, for J = 5, its angular momentum and angular velocity. Determine the energy absorbed in the J = 6 → J = 5 transition in cm^{-1} and erg/molecule.

Soln. The reduced mass of the OH-radical is given by

$$\mu_{OH} = \frac{M_0 M_H}{M_0 + M_H}$$

$$= \frac{(1\times16)(6.023\times10^{23})^2}{(1+16)(6.023\times10^{23})^2} = \frac{16}{17\times(6.023\times10^{23})} = 1.56\times10^{-24}\ gm$$

If I is the moment of inertia, then the internuclear distanec 'r' is:

$$r = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{1.48\times10^{-4}\ gm-cm^2}{1.56\times10^{-24}\,gm}}$$

$$= 0.97\times10^{-8}\ cm = 0.97\mathring{A}$$

The angular momentum is given by

$$L = \sqrt{J(J+1)}\,\frac{h}{2\pi}$$

For J = 5, we have

$$L = \sqrt{30}\times\frac{6.62\times10^{-37}}{2\times3.14}\ erg-\sec = 5.77\times10^{-27}\ erg-\sec$$

The corresponding angular velocity is:

$$\omega = \frac{L}{I}$$

$$= \frac{5.77\times10^{-27}\,erg-\sec}{1.48\times10^{-49}\,gm-cm^2} = 3.4010^{12}\ \sec^{-1}$$

The wave number of the radiation absorbed (absorbed energy in cm^{-1}) in transition from J to J+1 is given by

$$v = 2B(J+1)$$

Where J refers to the lower state. Therefore, for the transition $J = 6 \rightarrow J = 5$, we have

$$v = 2B(5+1) = 12B$$

But $B = \dfrac{h}{8\pi^2 Ic}$ $\therefore$ $v = \dfrac{12h}{8\pi^2 Ic}$

$$= \frac{12\times\left(6.62\times10^{27}\ erg-\sec\right)}{8\times(3.14)^2\times\left(1.48\times10^{-40}\ gm-cm^2\right)\left(\times10^{10}\ cm-\sec^{-1}\right)}$$

$$= 227\ cm^{-1}$$

The corresponding energy E in erg/molecule is obtained by

$$E = vhc$$

$$= \left(227\ cm^{-1}\right)\left(6.62\times10^{-27}\ erg-\sec\right)\left(3\times10^{10}\ cm-\sec^{-1}\right)$$

$$= 4.50\times10^{-14}\ erg\ /\ \text{molecule}$$

4. The $J = 1 \leftarrow 0$ transition in HCl occurs at 20.68 cm^{-1} regarding the molecule to be rigid rotator, calculate the wavelength of the transition $J = 15 \leftarrow 14$

Soln. The wave number of the radiation absorbed in a rotational from J to J+1 is given by

$$v = 2B(J+1)$$

For a transition from J = 0 to J = 1, we have

$$v = 2B$$

But $v = 20.68\ cm^{-1}$ (given)

$\therefore$ $2B = 20.68$

Or, $B = 10.34\ cm^{-1}$

Again, the wave number of the radiation absorbed in $J = 15 \leftarrow 14$ is given by

$v = 2B(J+1)$ where J refers to lower state.

$$= 2B(14+1)$$

$$= 30(1034) = 310.2\ cm^{-1}$$

The corresponding wavelength is

$$\lambda = \frac{1}{v} = \frac{1}{310.2}\ cm$$

$$= 32\times10^{-4}\ cm = 32\mu$$

5. The transition J = 3 to J = 4 in HCl is associated with radiation of 83.03 cm^{-1}. Use the rigid-rotation approximation to calculate the moment of inertia and internuclear distance of HCl.

Soln. The wave number of absorbed radiation in rotational transition $J \rightarrow (J+1)$ is given by

$$v = 2B(J+1)\ cm^{-1}$$

For $J = 3 \rightarrow J = 4$, we have

$$v = 2B(3+1) = 8B$$

But $v = 83.03\ cm^{-1}$ (given)

$\therefore$ $8B = 83.03\ cm^{-1}$

$$B = 10.38\ cm^{-1}$$

The rotational constant B is given by

$$B = \frac{h}{8\pi^2 Ic}$$

$\therefore$ The moment of inertia of the molecule is

$$I = \frac{h}{8\pi^2 Ic}$$

$$= \frac{6.62\times10^{-27}\ erg-\sec}{8\times(3.14)^2\times(10.38\ cm^{-1})(3\times10^{10}\ cm-\sec^{-1})}$$

$$= 2.7\times10^{-40}\ gm-cm^2$$

The reduced mass of HCl molecule is

$$\mu_{HCl} = \frac{M_H M_{Cl}}{M_H + M_{Cl}}$$

$$= \frac{(1\times35)(6.023\times10^{23})^2}{(1+35)(6.023\times10^{23})}$$

$$= 1.61\times10^{-24}\ gm$$

The internuclear distacne (bond length) is therefore

$$r = \sqrt{\frac{1}{\mu}}$$

$$= \sqrt{\frac{2.7\times10^{-40}\ gm-cm^2}{1.61\times10^{-24}\ gm}}$$

$$= 129\times10^{-8}\ cm = 1.29\mathring{A}$$

6. The far-infra-red spectrum of H^1Br^{79} cosists a series of lines spaced $17\ cm^{-1}$ apart. Find the internuclear distance of H^1Br^{79} $\left(h = 6.62\times10^{-27}\ erg-\sec\right)$ $\left(=3.0\times10^{10}\ cm/\sec\right)$, $N_A = 6.023\times10^{23}$

Soln. The wave number of the lines in a pure rotational spectrum are given by

$$v = 2B(J+1)$$

Where J refers to the lower rotational Q.No. The separation between two successive corresponding to J and J+1 is:

$$\Delta v = 2B(J+2) - 2B(J+1) = 2B$$

Here, $\Delta v = 17\ cm^{-1}$

$\therefore$ $2B = 17\ cm^{-1}$

$B = 8.5\ cm^{-1}$

The moment of inertia of the molecule is

$$I = \frac{h}{8\pi^2 Bc}$$

$$= \frac{6.62\times10^{-27}\ erg-\sec}{8\times(3.14)^2(8.15\ cm^{-1})(3\times10^{10}cm/\sec)}$$

$$= 3.29\times10^{-40}\ gm-cm^2$$

The reduced mass of H^1Br^{79} is:

$$\mu_{HBr} = \frac{(1\times 79)/\left(6.023\times 10^{23}\right)^2}{(1+79)/\left(6.023\times 10^{23}\right)} = 1.64\times 10^{-24}\ gm$$

$\therefore$ The internuclear distance is:

$$r = \sqrt{\frac{1}{\mu}}$$

$$= \sqrt{\frac{3.29\times 10^{-40}\ gm-cm^2}{1.64\times 10^{-24}\ gm}} = 1.42\times 10^{-8}\ cm = 1.42\mathring{A}$$

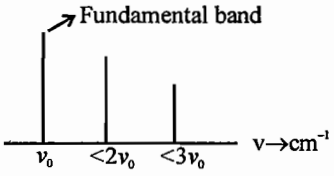
VIBRATIONAL ROTATIONAL SPECTRA

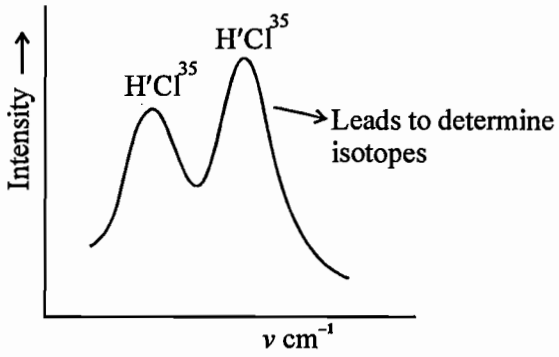
Salient features:

Observed in absorption only for hetronuclear molecules which have permanent dipole moment in near infrared region $\left(10^0 \le \lambda \le 10^2\,\mu m \;\&\; E \sim 10^{-1} eV\right)$. The dipole moment interacts with the field of the light and starts oscillating and it leads to the spectrum.

H_2, N_2, O_2: Homonuclear molecules as they do not have permanent dipole moment does not show this spectra.

In particle, vibrational-rotational spectra of a molecule like HCl consists of an intense band, knonw as fundamental band and a number of weak bands called overtones at wave numbers approximately double triple of fundamental band.





[Fine structure of fundamental band for (Hcl)

Explanation of vibrational rotational spectra:

To explain vibrational rotatinal spectra first we treated the molecule as a **Harmonic oscillator** of p.E.

$$(V) = \frac{1}{2}kx^2$$

And potential energy curve as perfectly parabolic. For it writing the schrocidinger time independent equation,

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V)\psi = 0$$

And solving it we obtain the energy levels of H.O. as

$$\boxed{E_v = \left(v + \frac{1}{2}\right)h\nu_{osc}}$$

Where $v = 0, 1, 2$ & ν_{osc} = frequency of oscillation $= \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$

where k = force constant.

and μ = reduce mass.

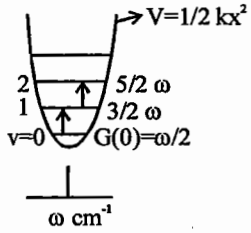
Energy in terms of wave number is:

$$G(v) = \frac{E_v}{hc} = \left(v + \frac{1}{2}\right)\frac{h\,\nu_{osc}}{hc} = \left(v + \frac{1}{2}\right)\frac{\nu_{osc}}{c}$$

Or, $\boxed{G(v) = \left(v + \frac{1}{2}\right)\omega\ cm^{-1}}$, $\omega = \frac{\nu_{osc}}{c}$ = vibrational constant

putting $v = 0, 1, 2...$

$$G(v) = \frac{1}{2}\omega, \frac{3}{2}\omega, \frac{5}{2}\omega.....$$



The selection rule $\boxed{\Delta v = \pm 1}$

gives only one band at wave number.

$$G(v+1) - G(v) = \omega\left(v + \frac{3}{2}\right) - \omega\left(v + \frac{1}{2}\right)$$

$$= \omega\ cm^{-1}$$

Which does not matches what we observe practically. Therefore, we have to change our consideration of diatomic molecule as a harmonic oscillator to anharmonic oscillator.

Molecule as Anharmonic oscillator:

Taking the P.E. $(V) = fx^2 - gx^3$.

Where g<<f we obtain the energy levels of anharmonic oscillator in terms of wave number is:

$$\boxed{G(v) = \omega_e\left(v + \frac{1}{2}\right) - \omega_e x_e\left(v + \frac{1}{2}\right)^2}$$

Where $\omega_e = \frac{v_{osc}}{c}$ = vibrational constant.

$\omega_e x_e$ = Anharmonic constant and small but positive

Now, $G(0) = \frac{\omega_e}{2} - \frac{\omega_e x_e}{4}$

$$G(1) = \frac{3}{2}\omega_e - \frac{9}{4}\omega_e x_e$$

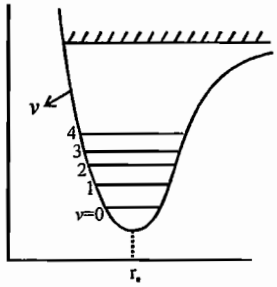
$$G(2) = \frac{5}{2}\omega_e - \frac{25}{4}\omega_e x_e$$

$$G(3) = \frac{7}{2}\omega_e - \frac{49}{4}\omega_e x_e$$

.....

.....

.....



$$G(1) - G(0) = \omega_e - 2\omega_e x_e$$

$$G(2) - G(1) = \omega_e - 4\omega_e x_e$$

$$G(3) - G(2) = \omega_e - 6\omega_e x_e$$

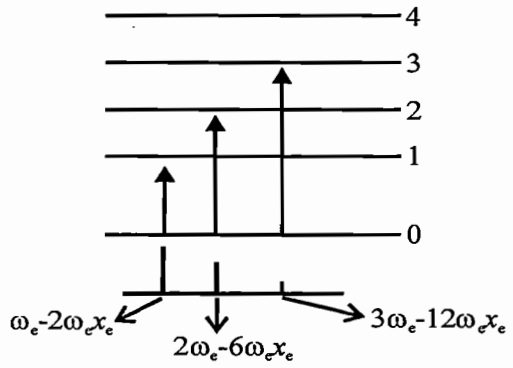
Thus the separation between energy levels decreases with increasing of v.

Now selection rules are

$\boxed{\Delta v = \pm 1, \pm 2, \pm 3.....}$

The wave number of fundamental band

$$G(1) - G(0) = \omega_e - 2\omega_e x_e$$



And first overtime is

$$G(\mathrm{v})-G(0)=2\omega_e 6\omega_e x_e$$

And thrid overtone $=G(3)-G(0)=3\omega_e-12\omega_e x_e$

Thus the wave number of overtones are slightly less than the twice, thrice,fundamaental band. the wave number of fundamental band, which is according to the practical observation.

- **Fine structure of IR bands: Molecule as vibrating rotator:**

In case of vibrating rotator, the energy in terms of wave number is given as

$$G(\mathrm{v})+F(J)=G(\mathrm{v})+BJ(J+1)$$

Where $B=\dfrac{h}{8\pi^2 Ic}=\dfrac{h}{8\pi^2\mu r^2 c}$ is not const. here because as the molecule vibrates recharges and B is not constt.

$\therefore \quad G(\mathrm{v})+F(J)=G(\mathrm{v})+B_{\mathrm{v}}J(J+1)$

$\therefore$ We will write B_v and rather B.

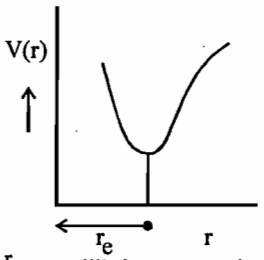
Let us discuss the fine structure of fundamental band in which the lower vibrational state $\mathrm{v}''=0$ and uper vibrational state $\mathrm{v}'=1$ and $\Delta \mathrm{v}=\pm 1$. There are many rotational levels corresponding to eac vibrational level. Let J'' and J' be the rotational levels corresponding to $v''=1$ and $v'=1$ respectively as shown in fig. 1 below.

$B_{v''} > B_{v'}$ [as v' is higher static and in it more vibrational even and more).

$$B_{\mathrm{v}}=B_e-\alpha_e\left(v+\frac{1}{2}\right)$$

$$B_e=\frac{h}{8\pi^2\mu r_e^2 c}$$

$v=0,1,2.....\&\ \alpha_e=$ constant



r_e = equilibrium separations and is small but +i've

[As $B_{v''} > B_{v'}$ is rotational levels of v'' are more seperated then v']

Now the selection rule at J are

$$\boxed{\Delta J=\pm 1}$$

Thus, we get two branches of rotational lines of wave number.

$$v=G(\mathrm{v}')-G(\mathrm{v}'')+B_{\mathrm{v}'}+J'(J'+1)-B_{\mathrm{v}}''J''(J''+1)$$

R-Branch: For it, $\Delta J=+1=J'-J'' \quad \Rightarrow \quad J'=J''+1$

Thus the wave number of R branch is:

$$v_R=\left[G(v')+B_{v'}\,J'(J'+1)\right]-\left[G(v'')+B_{v''}J''(J''+1)\right]$$

$$\left[G(v')-G(v")\right]+B_{v'}(J"+1)(J"+2)-B_{v"}J"(J"+1)$$

$$v_R = v_0 + 2B_{v'} + (3B_{v'} - B_{v"})J" + (B_{v'} - B_{v"})J"^2$$

P-Branch: For it $\Delta J = J' - J" = -1 \Rightarrow J' = J" - 1, J" = 0,1,2,...$& we get liens R(0), R(1)...

$\therefore$ Wave number of p-branch is:

$$v_p = \left[G(v') + B_{v'} J'(J'+1)\right] - \left[G(v") + B_{v"} J"(J"+1)\right]$$

$$= \left[G(v') - G(v")\right] + B_{v'}(J"-1)(J") - B_{v"}(J")(J"+1)$$

$$v_p = v_0 - (B_{v'} + B_{v"})J" + (B_{v'} - B_{v"})J"^2$$

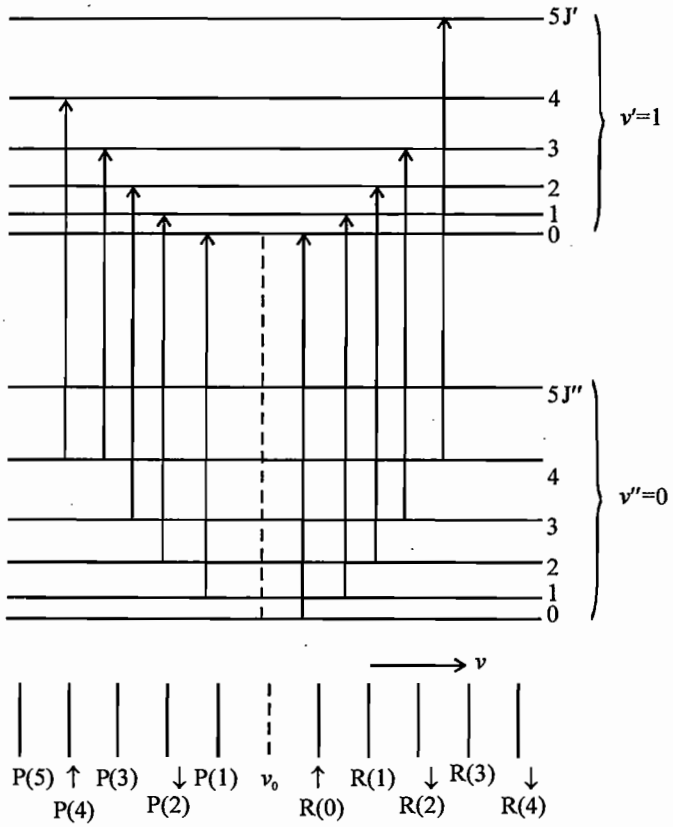
Where $J" = 1,2,3.....$& we get lines P(1), P(2)

Q-Branch: $\Delta J = 0$, obtain only for no (Nitrous oxide).

We can also write

$$\boxed{v_{PR} = v_0 + (B_{v'} + B_{v"})m + (B_{v'} - B_{v"})m^2}$$, Where $m = J"+1 = 1,2,3.....$ for R(0), R(1) ..... lines

And $m = -J" = -1, -2.....$ for p lines P(1), P(2) ..... lines.



Problems:

1. The force constant of the bond in CO molecule is 1870 N/m. Calculate the frequency of vibrational of the molecule and spacing between its vibrational energy levels in eV. Given that reduced mass of $CO = 1.14\times10^{-28}\ kg$, $h = 6.63\times10^{-27}$ erg-sec and $1\,eV = 1.60\times10^{-27}\ erg$.

Soln. Frequency of vibration of the molecule is

$$\nu_{osc} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

$$= \frac{1}{2\times3.14}\sqrt{\frac{1870\ N/m}{1.14\times10^{-26}\,kg}}$$

$$= 6.45\times10^{13}\ /\sec$$

Vibrational energy of a diatomic molecule is

$$E_V = h\,V_{osc}\left(V+\frac{1}{2}\right) \qquad v = 0,1,2.....$$

The separation between two successive vibrational energy level is:

$$\Delta E = E_{V+1} - E_V$$

$$= h\nu_{osc}\left(V+\frac{3}{2}\right) - h\nu_{osc}\left(V+\frac{1}{2}\right)$$

$$= h\,\nu_{osc}$$

$$= \left(6.63\times10^{-27}\ erg-\sec\right)\left(6.45\times10^{13}\ s^{-1}\right)$$

$$= 42.76\times10^{-14}\ erg$$

$$= \frac{42.76\times10^{-14}}{1.60\times10^{-12}} = 26.\times10^{-2}\ eV$$

2. In the near I-R spectrum of HCl molecule there is a single intense band at $2885.9\ cm^{-1}$. Assuming that it is due to the transition between vibrational levels, show that the force constant k is $4.8\times10^{5}\ dyne/cm$. (Given: $\mu = 1.68\times10^{-24}\ gm$).

Soln. The wave number of the fundamental vibrational band is ω, the vibrational constant of the molecule. Thus

$$\omega = 2885.9\ cm^{-1}$$

But $\omega = \frac{\nu_{osc}}{c}$, where ν_{osc} is the fundamental frequency of vibration

Now,

$$\nu_{osc} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$, where k is the force constant.

And μ is the reduced mass of te molecule.

$\therefore\quad k = 4\pi^2\mu\nu_{osc}^2 = 4\pi^2\mu\omega^2c^2$ ... (1)

The reduced mass of H^1Cl^{35} is given by

$$\mu = \frac{M_H M_{Cl}}{M_H + M_{Cl}}$$

$$= \frac{1\times 35}{1+35} M_H = \frac{35}{36}\times 1.68\times 10^{-24}\ gm$$

$$= 1.63\times 10^{-24}\ gm$$

Substituting the values of μ, ω & c in equation (1)

$$k = 4\times(3.14)^2\times\left(1.63\times 10^{-24}\ gm\right)\times\left(2885.9\ cm^{-1}\right)^2\times\left(3\times 10^{10}\ cm\sec^{-1}\right)^2$$

$$= 4.8\times 10^5\ dyne/cm$$

3. Calculate the amplitude of the vibrations in the $v = 0$ level of the molecule ω which has a stiff bond of $18.7\times 10^5\ dyne/cm$ $\left(h = 6.63\times 10^{-27} erg - s\right)$

Soln. Given $k = 18.7\times 10^5\ dyne/cm$

Let x_0 be the max. displacement (amplitude) from the equilibrium position. The P.E. at $x = x_0$ is equal to the vibrational energy to the $v = 0$ state.

i.e.

$$\frac{1}{2}kx_0^2 = \frac{1}{2}hv_{osc}$$

$$\therefore \qquad x_0 = \sqrt{\frac{hv_{osc}}{k}} \qquad \ldots (1)$$

$$v_{osc} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

Where μ is the reduce mass of the molecule.

The reduced mass of the $C^{12}O^{16}$ molecule is given by

$$\mu = (12\times 6)/\left(6.023\times 10^{23}\right)^2 = 11.4\times 10^{-24}\ gm$$

$$(12+16)/\left(6.023\times 10^{23}\right)$$

$$\therefore \qquad v_{osc} = \frac{1}{2\times 3.14}\sqrt{\frac{18.7\times 10^5\ dyne/cm}{11.4\times 10^{-24}\ gm}}$$

$$= 6.45\times 10^{13}\ \sec^{-1}$$

Putting this value in equation (1), we get

$$x_0 = \sqrt{\frac{\left(6.63\times 10^{-27}\ erg - \sec\right)\left(6.45\times 10^{18}\ \sec^{-1}\right)}{18.7\times 10^5\ dyne/cm}}$$

$$= 4.78\times 10^{-10}\ cm$$

$$= 4.78\times 10^{-2}\ \mathring{A}$$

4. The values of ω_e 4395, 3817 and 3118 cm^{-1} for H_2. HD and D_2 molecules respectively. Calculate their approximate zero-point energies in Kcal/mole. The values of $\omega_e x_e$ are 118, 95 and 64 cm^{-1} for the same molecules. Calculate the exact zero point energies.

Soln. The approximate term value for the molecule are given by

$$G(v) = \omega_e\left(v+\frac{1}{2}\right)$$

The zero-point energy corresponding to $v = 0$ is,

$$\therefore \quad G(0) = \frac{1}{2}\omega_e$$

For $H_2, \omega_e = 4395\ cm^{-1}$

$$\therefore \quad G(0) = \frac{1}{2} \times 4395 = 2197.5\ cm^{-1}$$

$1\ cm^{-1} = 2.86 \times 10^{-3}\ k\ cal/mole$

$$\therefore \quad G(0) = 2197.5\left(2.86 \times 10^{-3}\right)$$

$$= 6.28\ k\ cal/mole$$

Similarly, for HD $G(0) = 5.45\ kcal\ /\ mole$

for $D_2, G(0) = 4.46\ kcal\ /\ mole$

Now,
The more accurate term values are given by

$$G(\mathrm{v}) = \omega_e\left(v + \frac{1}{2}\right) - \omega_e x_e\left(v + \frac{1}{2}\right)^2$$

$$G(0) = \frac{1}{2}\omega_e - \frac{1}{4}\omega_e x_e$$

For $H_2, \omega_e = 4395\ cm^{-1}$ & $\omega_e x_e = 118\ cm^{-1}$

$$\therefore \quad G(0) = \frac{1}{2} \times 4395 - \frac{1}{4} \times 118$$

$$= 2197.5 - 29.5 = 2168\ cm^{-1}$$

$$= 2168 \times \left(2.86 \times 10^{-3}\right) = 6.20\ kcal/mole$$

Similarly,

For HD, $G(0) = 5.39\ kcal\ /\ mole$

$D_2, G(0) = 4.41\ kcal\ /\ mole$

5. The fundamental band for CO is centered at $2143.3\ cm^{-1}$ and the first overtone at $4259.7\ cm^{-1}$. calculate $\omega_e, \omega_e x_e$, the vibrational frequency and the simple harmonic force constant.

Soln. The vibrational terms of a diatomic molecule are given by

$$G(\mathrm{v}) = \omega_e\left(v + \frac{1}{2}\right) - \omega_e x_e\left(v + \frac{1}{2}\right)^2$$

$$G(0) = \frac{1}{2}\omega_e - \frac{1}{4}\omega_e x_e$$

$$G(1) = \frac{3}{2}\omega_e - \frac{9}{4}\omega_e x_e$$

$$G(2) = \frac{5}{2}\omega_e - \frac{25}{4}\omega_e x_e$$

For the wave number of fundamental band $1 \rightarrow 0$,

We have

$$v = G(1) - G(0)$$

$$= \omega_e - 2\omega_e x_e = 2143.3\ cm^{-1} \quad \ldots (1)$$

For the first overtone band $2 \rightarrow 0$, We have

$$v = G(2) - G(0)$$

$$2\omega_e - 6\omega_e x_e = 4259.7\ cm^{-1} \quad \ldots (2)$$

Solving equation (1) and (2), we get

$$\omega_e = 2170.0\ cm^{-1}$$

$$\omega_e x_e = 13.45\ cm^{-1}$$

The vibrational frequency is:

$$v_{osc} = C\omega_e = \left(3 \times 10^{10}\ cm/\sec\right)\left(2170.2\ cm^{-1}\right)$$

$$= 6.51 \times 10^{13}/\sec$$

The S.H. force constant is:

$$k = 4\pi^2 \mu v_{osc}^2$$

$$= 4(3.14)^2 \left(\frac{6.85841}{6.0251 \times 10^{25}}\right)\left(6.51 \times 10^{13}\right)^2$$

$$= 1.90 \times 10^6\ dyne/cm$$

6. The fundamental mode of HCl occurs at a $2886 cm^{-1}$, predict the frequency of the corresponding mode of DCl.

Soln. The difference in frequency arises due to difference in mass of the isotopic molecules, we have

$$v_{osc} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

k is same for both the molecules as it is determined by electronic motion. If ω^i stands for the heavier isotope, then

$$\frac{\omega^i}{\omega} = \frac{v_{osc}^i}{v_{osc}} = \sqrt{\frac{\mu}{\mu^i}} = \rho\,(say)$$

$$\omega^i = \rho\omega$$

So that $\rho = \sqrt{\frac{\mu_{HCl}}{\mu_{DCl}}} = \sqrt{\frac{(1\times35)/(1+35)}{(2\times35)/(2+35)}} = \sqrt{\frac{35}{36}\times\frac{37}{70}}$

$$\sqrt{\frac{37}{72}} = 0.7168$$

Treating the molecule as a harmonic oscillater the fundamental band occurs at $\omega\ cm^{-1}$, where ω is the vibrational constant. Here $\omega = 2886\ cm^{-1}$. For HCl.

$\therefore$ The fundamental band for DCl occurs at ω^i where,

$$\omega^i = \rho\omega = 0.7168 \times 2886\ cm^{-1} = 2069\ cm^{-1}$$

7. If the fundamental band H^1Cl^{35} lies at 3.46μ. Calculate the wavelength of the corresponding of H^2Cl^{37}.

Soln. If i stands for the heavier isotope, then

$$\frac{\omega^i}{\omega} = \sqrt{\frac{\mu}{\mu_i}} = \rho$$

Or, $\omega^i = \rho.\omega$

In terms of wavelength, we write

$$\lambda^i = \frac{1}{\rho}\lambda$$

$$\rho = \sqrt{\frac{(1\times35)/(1+35)}{(2\times37)/(2+37)}} = \sqrt{\frac{35}{36}t\frac{39}{74}} = 0.7158$$

$\lambda = 3.46$ microns

$$\lambda^i = \frac{3.46 \text{ microns}}{0.7158} = 4.83 \text{ microns}$$

8. The $2886\ cm^{-1}$ fundamental band of the HCl can be shown to fit in the empirical equation.

$v(cm^{-1}) = 2885.90 + 20.577m - 0.3034m^2$. Calculate the value of $B_e, B_0, \& B$, Given $\alpha_e = 0.3019\ cm^{-1}$

Soln. The general equation for the rotational lines to a band is:

$$v = v_0 + (B_{v'} + B_{v''})m + (B_{v'} - B_{v''})m^2$$

Comparing it with the given equation for the fundamental $(v'' = 0, v' = 1)$, band, we have

$$B_1 + B_0 = 20.577\ cm^{-1}$$

$$B_1 - B_0 = -0.3034\ cm^{-1}$$

Solving, we get

$$B_1 = 10.1368\ cm^{-1}$$

$$B_0 = 10.4402\ cm^{-1}$$

And

We know the rotational constant corresponding to the vibrational state v is given by

$$B_v = B_e - \alpha_e\left(v + \frac{1}{2}\right)cm^{-1}$$

For the $v = 0$ state, we would have

$$B_0 = B_e - \frac{1}{2}\alpha_e$$

$$B_e = B_0 + \frac{1}{2}\alpha_e$$

$$= 10.4402 + \frac{1}{2}(0.3019)\ cm^{-1}$$

$$= 10.5909\ cm^{-1}$$

RAMAN SPECTRA

- **Nature of the Raman effect:**

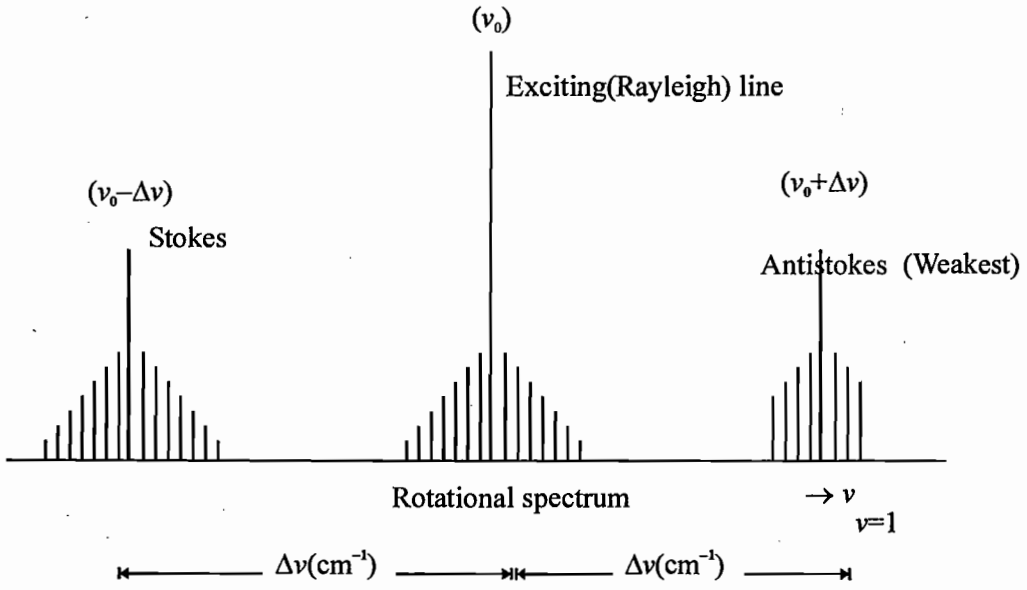
Raman effect was discovered by C.V. Raman in 1928 and he got nobel prize for it in 1930°. When a strong beam of visible or U-V line spectral light illuminates a gas, a liquid or a transparent solid a small fraction of light is scattered in all directions. The spectrum of the scattered light is found to consist of lines of the same frequencies as the incident beam (Rayleigh lines) and also additional lines, called "Raman lines". The Raman lines corresponding to each exciting (Rayleigh) line occur symmetically on both side of the exciting line.

- The lines on the low frequency side of the exciting are called **"Stokes lines"** while those on the high-frequency side are called **"Anti-stokes lines".**
- The antistokes Raman lines are much weaker than the stokes Raman lines.

The displacement (in cm^{-1}) of the Raman lines from the corresponding exciting lines are independent of the frequencies of the light. If another light source with a different line-spectrum is used, other Raman lines are obtained for the same scattering substance. However, the displacements (Δv) from the excitting lines are the same.

For different scattering substances, the displacements have different magnitudes. Thus, the Raman displacement are characteristic of the scattering substance.

The typical Raman spectrum of a diatomic gas is shown in fig.



If the wave number is v_0 for Rayleigh line, then wave number for stokes Raman lines $= v_0 - \Delta v$, and the wave number of anti stokes Raman lines $= v_0 + \Delta v$.

$$\left[v_0 = \frac{1}{\lambda_0}\right]$$

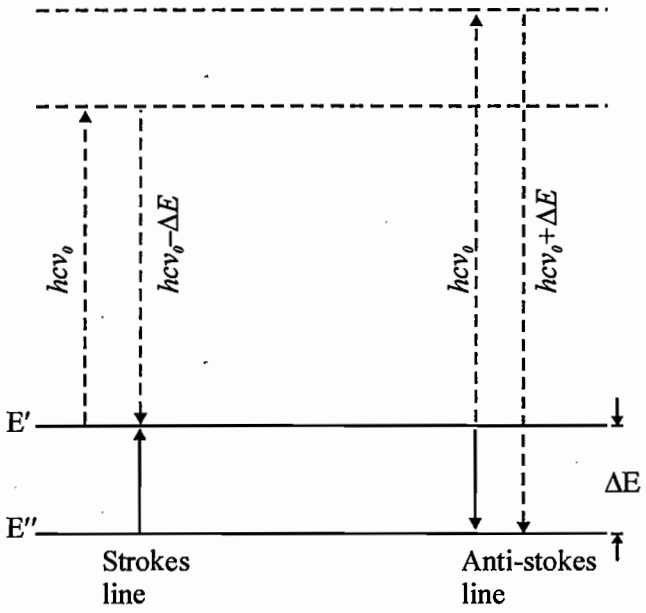
[E decreases, frequency decreases, wave number decrease, λ increases).

- **Quantum theory of Raman effect:**

According to the quantum explanation of Raman effect when an incident photon of energy (hcv_0) (where is v_0 isthe wave number) collides with a scatterer molecule initially in a stationary state E", the total energy $hcv + E"$ remains conserved. If the collision is elastic, the molecule remains in its initial energy state, and the photon is

scattered with its energy unchanged giving rise to the Rayleigh line at wave number (ν_0). The collision may however be inelastic as well when there is an exchange of energy between the photon and the molecule. The molecule in the initial state E'' take energy from the photon and goes to a higher energy E', and the photon is consequently scattered with a smaller energy $hc\nu_0 - \Delta E$ where $\Delta E = E' - E''$. This gives rise to a Raman line with a frequency less than that of the incident spectral line at a wave number $\frac{hc\nu_0 - \Delta E}{hc}$, the wave number shift being $\frac{\Delta E}{hc}$.

Such a Raman line is called a 'Stokes line".



If, on the other hand, the molecule was initially in a higher state E' and transferred to E'' by collision, the scattered photon emerges with increased energy $(hc\nu_0 + \Delta E)$. This gives rise to a Raman line with a frequency greater than that of the incident spectral line at a wave number $\frac{hc\nu_0 + \Delta E}{hc}$, the wave number shift again being $\frac{\Delta E}{hc}$ such a Raman line is called an **"Anti-stokes line".** Thus stokes and anti-stokes Raman lines are symmetrically situated on either side of the Rayleigh line. The Raman-shfits $\Delta\nu = \frac{\Delta E}{hc}$ gives directly the energy difference between the stationary states of the molecule. As the number of molecules in lower energy states are more, therefore more probability will be of the transitions of molecules from E'' to E' and hence have more stokes lines and therefore more intensity than anti-stokes lines.

PROBLEMS:

1. The exciting line in an experiment is of 5460 Å and the stokes line is at 5520 Å. Find the wavelength of the anti-stokes line.

Soln. The stokes and anti-stokes lines have the same wave number displacement w.r.t the exciting line. The wave number of the exciting line is $\left(v=\frac{1}{\lambda}\right)$ $\quad 1\mathring{A}=10^{-8}\ cm$

$$v=\frac{1}{5460\times10^{-8}}cm=18315\ cm^{-1}$$

And that of he stokes line is $\frac{1}{5520\times10^{-8}}cm=18116\ cm^{-1}$

The wave number displacement is, $\Delta v=18315-18116\ cm^{-1}$

$$=199\ cm^{-1}$$

$\therefore$ The wave number corresponding to the anti-stokes lines would be given by

$$v+dv=18315+199=18514\ cm^{-1}$$

And the corresponding wavelength is

$$\lambda=\frac{1}{18514}cm^{-1}=5.401\times10^{-5}\ cm=5401\mathring{A}$$

2. A substance shows a Raman line at 4567 Å when exciting line 4358 Å is used. Deduce the poistions of stokes and anti-stokes lines for the same substances when the exciting line 4047Å is used.

Soln. The wave number corresponding to the exciting line 4358Å is:

$$v=\frac{1}{4358\times10^{-8}}cm=22946\ cm^{-1}$$

And that corresponding to the Raman line at 4567 Å is $\frac{1}{4567\times10^{-8}}cm=21896\ cm^{-1}$

$\therefore$ The wave-number displacement is

$$\Delta v=22946-21896=1050\ cm^{-1}$$

Note: The Raman displacement is the characteristic of the substance whichever be the exciting line).
Now the wave number corresponding to the exciting line 4047 Å is:

$$v=\frac{1}{4047\times10^{-8}}cm=24710\ cm^{-1}$$

$\therefore$ The wave number for the stokes and 25760 cm^{-1} lines are
The corrresponding wavelength are

$$\lambda_{stokes}=\frac{1}{23660\ cm^{-1}}=4.2265\times10^{-5}\ cm=4226.5\mathring{A}$$

$$\lambda_{anti\text{-}stokes}=\frac{1}{25760}cm^{-1}=3.882\times10^{-5}\ cm=3882\mathring{A}$$

3. In the rotational Raman spectrum of HCl, displacement from the exciting line are represented by

$$\Delta v=\pm\left(62.4+41.6J\right)cm^{-1}$$

Calculate the moment of inertia of the HCl molecule $\left(h=6.62\times10^{-27}\ erg-\sec\right)$

$$c=3\times10^{10}\ cm/\sec$$

Soln. The rotational Raman displacement are given by

$$\left|\Delta v\right|^{r}_{Raman}=\left(62.4+41.6\,J\right)=41.6\left(J+\frac{3}{2}\right)$$

Comparing it with the theoritical formula

$$|\Delta v|^{r}_{\text{Raman}} = 4B\left(J+\frac{3}{2}\right)$$

$$4B = 41.6$$

$$= 10.4\ cm^{-1}$$

The rotational constant of the molecule is given by

$$B = \frac{h}{8\pi^2 IC} = \frac{h}{8\pi^2 IC}$$

Where I is the moment of inertia of the molecule

$$I = \frac{h}{8\pi^2 BC}$$

$$= \frac{6.62\times10^{-27}\ erg-\text{sec}}{8\times(3.14)^2\left(10.4\ cm^{-1}\right)\left(3\times10^{10}\ cm/\text{sec}\right)}$$

$$= 2.7\times10^{-40}\ gm-cm^2$$

RAMAN EFFECT

Discovered by C.V. Raman in 1928 and won nobel prize in 1930.

- **Nature of Raman Spectran: Molecular spectra**

Wave number of Rayleigh (excitting line or incident monochromatic light)

$$= \boxed{v_0 = \frac{1}{\lambda_0}}\ cm^{-1}$$

Wave number of stokes Raman line $= \left(v_0 - \Delta v\right) cm^{-1}$ and wave number of antistokes Raman line

$= \left(v_0 + \Delta v\right) cm^{-1}$

Δv is fixed for a susbtance.

- **Intensity of Rayleigh line > Intensity of stokes line > Intensity of anti-stokes Raman line:**

- The change in the energy of the molecule is eitehr of vibrational energy or rotational energy. Therefore, Raman spectra is of two kind.
(i) Vibrational Raman spectrum
(ii) Pure rotational Raman spectrum.

(i) Vibrational Raman spectrum:

The selection rule is

$$\Delta v = 0, \pm 1$$

$\Delta v = 0$ leads to Rayleigh line

$\Delta v = \pm 1$ leads to stokes and antistokes raman lines.

$$\therefore \quad v_v^{\text{Raman}} = v_0 \pm \left[G\left(v+1\right) - G\left(v\right)\right]$$

$$= v_0 \pm \left[\omega\left(v+\frac{3}{2}\right) - w\left(v+\frac{1}{2}\right)\right]$$

$$v_v^{\text{Raman}} = v_0 + \pm\omega$$ (+ sign for antistokes and –sign for stokes Raman line)

$$\therefore \quad \left|\Delta v_v^{\text{Raman}}\right| = \omega$$

Vibrational Raman shift.

For anharmonic treatment $\left|\Delta v_v^{\text{Raman}}\right| = \left(\omega_e - 2\omega t\, x_e\right)$

(ii) Rotational Raman spectrum selection rule are

$\Delta J = 0, \pm 2$

$\Delta J = 0$, For Rayleigh line.

$\therefore \quad v_{rot.}^{\text{Raman}} = v_0 \pm \left[F(J+2) - F(J)\right]$ & $\Delta J = \pm 2$ for stokes and antistokes line

$= v_0 \pm \left[B(J+2)(J+3) - BJ(J+1)\right]$ [as F(J) = B J(J+1)]

$= v_0 \pm (4BJ + 6B)$

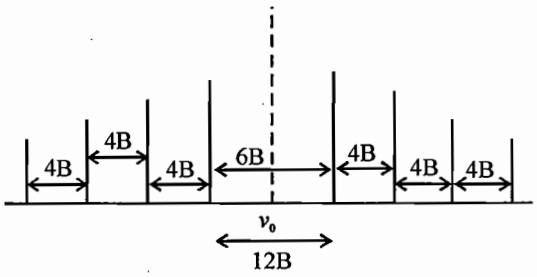
$$\boxed{v_{\text{rot.}}^{\text{Raman}} = v_0 \pm 4B\left(J + \frac{3}{2}\right)}$$

+ sign for antistokes Raman line and –ive for Raman lines

$$\left|\Delta v_{rot.}^{Raman}\right| = 4B\left(J + \frac{3}{2}\right)$$

$J = 0, 1, 2.....$

$v_{rot.}^{\text{Raman}} = v_0 \pm 6B, 10B, 14B, 18B.....$



Stokes line	**Antistokes line**
High intensity	Low intensity line
Stronglines	Weak line

Use:

1. To find Moment of inertia
2. To find bond length.
3. If Molequle symmetric = Raman spectra.

Raman ⇒ Active

Infrared ⇒ Inactive.

Raman Shift:

$$\Delta v = \frac{\Delta E}{hc}$$

Rule of Mutual Exclusion:

A further extremely important general rule has been established whose operation may be exemplified by carbon dioxide. we can summarize our conclusions about the Raman and infra-red activities of the fundamental vibrations of this molecule in Table and we see that, for this molecule, no vibration is simultaneously active in both Raman and infra-red. The corresponding general rule is:

Rule of mutual exclusion:

If a molecule has a centre of symmetry then Raman active vibrations are infra-red inactive, and vice versa. If there is no centre of symmetry then some (but not necessarily all) vibrations may be both Raman and infra-red active.

The converse of this rule is also true, i.e. the observance of Raman and infra-red spectra showing no common lines implies that the molecule has a centre of symmetry, but here caution is necessary since, as we have already seen, a vibration may be Raman active but too weak to be observed. However, if some vibrations are observed to give coincident Raman and infra-red absorptions it is certain that the molecule has no centre of symmetry. Thus extremely valuable structural information is obtainable by comparision of the Raman and infra-red spectra substance.

Mode of vibration of CO_2	Raman	Infra-red
ν_1 : symmetric stretch	Active	Inactive
ν_2 : bend	Inactive	Active
ν_3 : asymmetric stretch	Inactive	Active

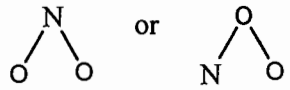
i.e. Structure of CO_2 is

O–C–O

Problem:

Both N_2O and NO_2 exhibit three different fundamental vibrational frequencies, and for the two molecules some modes are observed in both the infra-red and the Raman. The bands in N_2O show only simple PR structure (no Q branches) while those in NO_2 show complex rotational structure. What can be deduced about the structure of each molecule?

[**Hint:** Both molecules, no centre of symmetry. N_2O linear (PR bands); hence N–N–O. NO_2 non-linear; hence either.

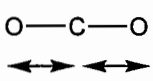


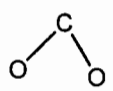
Problem:

With which type of spectroscopy wouldone observe the pure rotation spectrum of H_2? If the bond length of H_2 is 0.07417 nm, what would be the spacing of the lines in the spectrum?

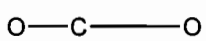
Ans. **Raman Spectroscopy.**

- $\frac{\text{Antistoke intensity}}{\text{Stoke intensity}} = e^{-whc/kT}$ **Intensity is population dependency.**
- **Nature of symmetry** $\Rightarrow$ **Raman** $\Rightarrow$ **Infrared inactive**
  $\Rightarrow$ **Infrared active.**





Bendmod



Assymetric bend

- Raman effect is successfully explained by Quantum mechanics. Classical mechanics fails to explain Raman effect.

Use of Raman effect.

Raman effect is used to determine the structure of diatomic molecules. By mutual exclusian principle "If the Infra red bands and Raman bands of a molecule not coincide the molecule will be linear and symmetric.".

Ex: CO_2, CS_2 Raman bonds donot coinside with IR bands. Therefore, their structure is

O–C–O, S–C–S

- **Difference between IR spectra and Raman spectra:**

IR spectra		Raman Spectra	
(i)	For showing IR spectra molecule must have permanent dipole moment	(i)	Molecule need not to have permanent dipole moment.
(ii)	Shown by hetronuclear molecules such as HCl, HBr, etc.	(ii)	Shown by homo as well as hetronuclear molecules.
(iii)	It is shown only when the energy of incident photon matches with the energy difference of two levels of molecule.	(iii)	It is not necessary here

Problem: The Raman spectrum of gaseous HBr is produced by means of a mercury lamp and a filter which only transmits the mercury lines 4358.3, 4046.6 and 4077.8Å. Raman lines are found at 4513.9, 4552.7 and 4905.1Å. Analyse this observation.

Ans. **[Each exciting line produces a stokes Raman line].**

ELECTRONIC SPECTRA: FRANCK-CONDON PRINCIPLE

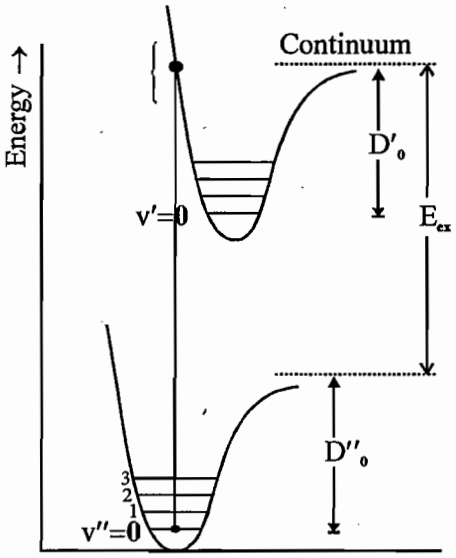
Salient Features of Molecular Electronic spectra:

Among the molecular spectra, the electronic spectra are the most complex which appear in the visible and ultraviolet regions, and involve a change in all the three electronic, vibrational and rotational energies of the molecule. Such spectra are studied both in emission and absorption, and the (electronic) bands show a fine structure more complicated than in the vibrational-rotational bands. The tendency of head formation is much stronger, and the bands may be degraded either towards the red or toward the violet.

All diatomic molecules exhibit electronic spectra. Homonuclear molecules (H_2, N_2, O_2) which give neither rotational nor vibrational-rotational spectra because they do not have permanent dipole moments, give electronic spectra because the instantaneous dipole moment* changes during the redistribution of electronic charge which accompanies the electronic transition.

Dissociation Energy and Dissociation Products:

$\overline{v}_{\text{continuum limit}=D''_0+E_{ex}}\ Cm^{-1}$



D'_0 =Dissociation energy of molecule in upper electronic state.

D''_0 = energy of $(0,0) + D'_0 - E_{ex}\ cm^{-1}$.

Problem: The absorption spectra of O_2 shows vibrational structure which becomes a continuum at 56876 cm^{-1}. The upper electronic state dissociate into one ground state dissociate into one ground state atom and one excited state atom (the excitation energy of which, measured from the atomic spectrum is 15875 cm^{-1}). Estimate the dissociation energy of ground state of O_2 in kJ/mole.

- **Rotational Fine Structure of Electronic-Vibration Transitions:**

To a very good approximation we can ignore centrifugal distortion and we have the energy levels of a rotating diatomic molecule as:

$$\varepsilon_{rot.} = \frac{h}{8\pi^2 Ic} J(J+1) = BJ(J+1)\ cm^{-1}\ \ (J = 0,1,2,.....)$$

$$\varepsilon_{total} = \varepsilon_{elec.} + \varepsilon_{vib.} + BJ(J+1)\ cm^{-1}$$

$$\Delta\varepsilon_{total} = \Delta\{\varepsilon_{elect.} + \varepsilon_{vib.}\} + \Delta\{BJ(J+1)\}\ cm^{-1}$$

$$\overline{v}_{spect.} = \overline{v}_{(v',v'')} + \Delta\{BJ(J+1)\}\ \ cm^{-1}$$

$$\Delta J = 0 \text{ or } \pm 1$$

$$J = 0 \not\longleftrightarrow J = 0$$

$$\nu_{spect.} = \bar{\nu}_{(\nu',\nu'')} + B'J'(J'+1) - B''(J''+1)\ cm^{-1}$$

1. P-branch: $\Delta J = -1,\ J'' = J' + 1$

$$\Delta\varepsilon = \bar{\nu}_P = \bar{\nu}_{(\nu',\nu'')} - (B' + B'')(J'+1) + (B' - B'')(J'+1)^2\ \ cm^{-1}$$

where $J' = 0, 1, 2....$

2. R-branch: $\Delta J = +1,\ J' = J'' + 1$

$$\Delta\varepsilon = \bar{\nu}_R = \bar{\nu}_{(\nu',\nu'')} + (B' + B'')(J''+1) + (B' - B'')(J''+1)^2\ \ cm^{-1}$$

Where $J'' = 0, 1, 2.....$

These two equations can be combined into:

$$\bar{\nu}_{P,R} = \bar{\nu}_{(\nu',\nu'')} + (B' + B'')m + (B' - B'')m^2\ cm^{-1}$$

Where $m = \pm 1, \pm 2.....$

3. Q-branch: $\Delta J = 0 \quad \Rightarrow \quad J' = J''$ But $J' = J'' \neq 0$

$$\bar{\nu}_Q = \bar{\nu}_{(\nu',\nu'')} + (B' - B'')m + (B' - B'')m^2$$

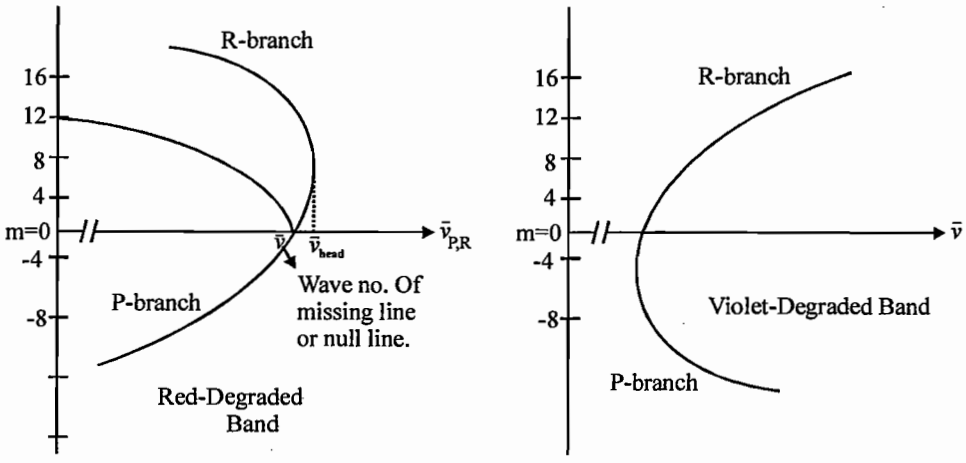
The Fortrat Diagram: As

$$\bar{\nu}_{P,R} = \bar{\nu}_{(\nu',\nu'')} + (B' + B'')m + (B' - B'')m^2\ cm^{-1}$$

m = 0 for band origin.

The value of m at which the vertex of fortrat parabola lies is at

$$\frac{d\bar{\nu}_{P,R}}{dm} = 0$$



$$m_{vertex} = -\frac{(B' + B'')}{2(B' - B'')}$$

$$\therefore \qquad \bar{\nu}_{head} = \bar{\nu} + (B' + B'')\left(-\frac{(B' + B'')}{2(B' - B'')}\right) + (B' - B'')\left(-\frac{B' + B''}{2(B' - B'')}\right)^2$$

$$\therefore \quad \bar{\nu}_{head} - \bar{\nu} = \frac{(B' + B'')}{4(B' - B'')}$$

If $\bar{\nu}_{head} - \bar{\nu}$ = +ive for a band degraded to the red and –ive for one degrated to the violet.

Problem: Rotational analysis of one band-system is given by

$$\bar{\nu} = 24762 + 25m - 2.1\, m^2 cm^{-1}$$

Deduce the position of the band-head, the values of B' and B" and the degradation of the band.

Problem: The fine-structure lines of CN band at 3883.4Å can be represented by the following equation:

$$\bar{\nu} = 25798 + 3.85\, m + 0.068\, m^2\ cm^{-1}$$

Calculate the separation between the null-line and the band-head and state the direction of degradation of the band.

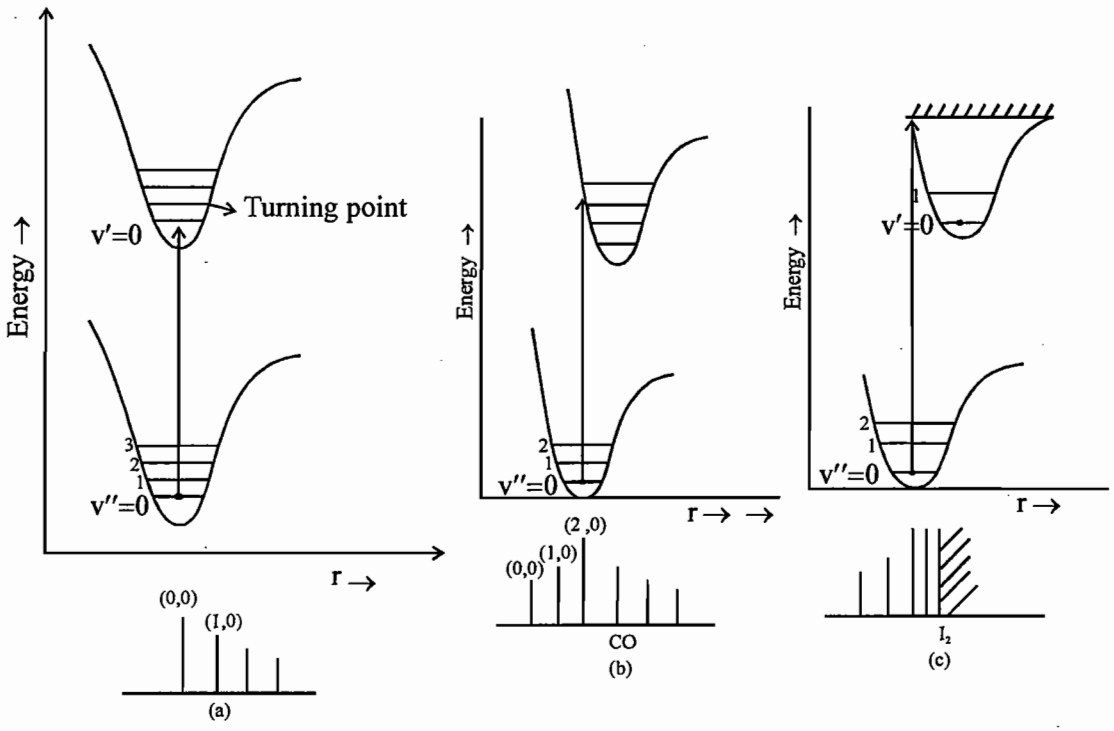
Franck Condon principle: Franck condon principle explaisn the variation of intensity among the bands of electronic band-system. The basic points of the Franck condon principle are:

1. An electronic transition in a molecule takes place so rapidly compared to the vibrational motion of the nuclei that the instantaneous internuclear distance and the velocity of the nuclei can be considered remaining unchanged during the electronic transition.

   This means that in diagrams showing the potential energy curves of the two electronic states, the transitions must be represented by "Vertical lines".

2. The most probable (most intense) vibrational transitions are those in which one of the two turning points of a vibrational level of one electronic state lies at approximately the same internuclear distance as one of the two turning points of a level of the other electronic state, except in case of v= 0 levels for which the mid-point rather than the turning point must be substituted.

Explanation of intensity distribution in absorption bands from Franck-condon principle:
Using the above two points the absorption transitions between two electronic states are shown in figure below.

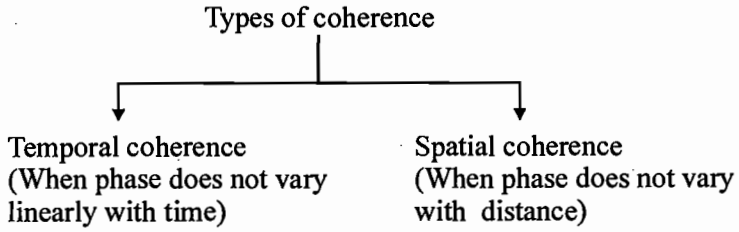


TEMPORAL AND SPATIAL COHERENCE

Coherence:

A wave which appears to be a pure sine wave for an infinitely long period of time, or in an infinitely extended space, is said to be a perfectly coherent wave. In such a wave there is a definite relationship between the phase of the wave at a given time and at a certain time later, or at a given point and at a certain distance away. No actual light source, however, emits a perfectly coherent wave. Light waves which are pure sine waves only for a limited period of time or in a limited space are partially coherent waves.

There are two different criteria of coherent; the criteria of time and the criteria of space. This gives rise to temporal coherence and spatial coherence.


Types of coherence
Temporal coherence
(When phase does not vary linearly with time)
Spatial coherence
(When phase does not vary with distance)

- **Coherence time (τ) coherence length:** The average time interval for which definite phase relationship exists is known as coherence time (τ) of the light beam. The distance (L) for which the field is sinusoidal is given by

$$L = \tau c$$

c = speed of light, L = coherence length.

- Temparal coherence is related with monochromaticity of spectral line:

If wavelength spread is $\Delta\lambda$ i.e. the light beam consist of all wavelength lying between λ & $\lambda + \Delta\lambda$

Then $$\boxed{L = \frac{\lambda^2}{\Delta\lambda}}$$

If $\Delta\lambda = 0$

L = infinite, τ = infinite

Perfectly temporal coherence.

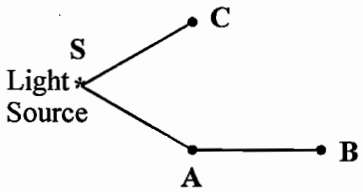
In terms of frequency.

$$\Delta\nu = \frac{c}{\lambda^2}\Delta\lambda \qquad [\text{as } \nu = \frac{c}{\lambda}, \Delta\nu = \frac{c}{\lambda^2}\Delta\lambda,]$$

$$\Rightarrow \boxed{\Delta\nu = \frac{c}{L} = \frac{1}{\tau}}$$

i.e. longer is the coherence time, the smaller is the frequency spread.

- Spatial coherence:



If AB<<L (coherence length)

Relationship between the points A and B.

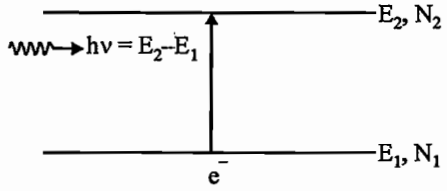
Is A, C are equidistant from S and if S is true point source, then the waves shall reach the ponits A and C in exactly the same phase.

Spatial coherence is related to the size of the source T_0 obtain a spatially coherent beam size of the source must be small in size.

LASERS

Light amplification by stimulated emission of radiations. These are three phenomenons

1. **Absorption of the radiation (Induced Process)**

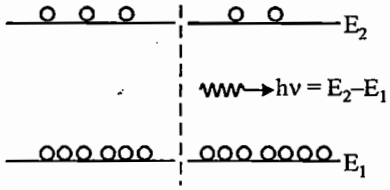


Atom is excited.

(a) Normal excited state (life time ~ 10^{-8} sec)

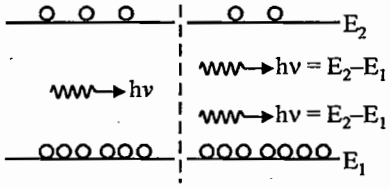
(b) Metastable state (life time >l 10^{-3}s or ~ 1 m sec or more than 1 m sec)

2. **Spontaneous Emission** (From normal excited states)



[Don't have any phase relationship]

3. **Stimulated Emission** (Induced metastable state)



[Don't have any phase relationship]

Transition Rate

Let number of atoms in the excited state $E_2 = N_2$

Let number of atoms in the ground state $E_1 = N_1$

Rate of absorption (No. of absorption / unit time) = $\nu = B_{12}N_1u(\nu)$ ... (1)

Where B_{12} = Einstein coefficient and this is the characteristics of particular energy level.

$u(\nu)$ = Energy density Energy of radiation per unit volume

Now, atoms can dexcited into lower-level by emitting radiation. This may be spontaneous or stimulated

Spontaneous transition rate = $A_{21} N_1$ ... (2)

If there is only spontaneous transition (Decrement of excited atoms) –ve sign

$\frac{dN_2}{dt} = -A_{21} N_2$, negative sign indicates that N_2 decreases due to the transition.

$\boxed{A_{21} = \frac{1}{t_{sp}}}$ sec^{-1}, $t_{sp} \rightarrow$ life time of excited state, sp stands for spontaneous.

A_{21} is also called Einstein's coefficeint.

$\frac{dN_2}{N_2} = -\frac{dt}{T_{sp}}$ $\quad T_{sp} = t_{sp}$

$\ln N_2(t) = -\frac{t}{t_{sp}} + c$

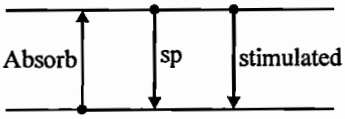
At time $t = 0$, $N_2(0)$, $\quad c = \ln N_2(0)$

$$N_2(t) = N_2(o)e^{-t/t_{sp}} \quad \text{... (3)}$$

Life time more $\Rightarrow$ slow decay

Rate of stimulated emission = $N_2 B_{21} u(\nu)$ ... (4)

Under thermal equilibrium



Rate of change in number of excited atoms must be zero.

$N_1 B_{12} u(\nu) - N_2 A_{21} - N_2 B_{21} u(\nu) = 0$

$$u(\nu) = \frac{A_{21}}{\frac{N_1}{N_2}B_{12} - B_{21}} \qquad \text{But } B_{12} = B_{21}$$

$$u(\nu) = \frac{A_{21}}{B_{21}\left[\frac{N_1}{N_2} - 1\right]} \quad \text{.... (5)}$$

According to Boltzmann distribution law $\frac{N_1}{N_2} = e^{\frac{E_2 - E_1}{kT}} = e^{\frac{h\nu}{kT}}$

$$u(\nu) = \frac{A_{21}}{B_{21}[e^{h\nu/kT} - 1]} \quad \text{.... (6)}$$

Energy density $u(\nu) = \frac{8\pi h \nu^3}{c^3}\left(\frac{1}{e^{h\nu/kT} - 1}\right)$ ... (7)

$$\frac{8\pi kT\nu^2}{c^3} = \frac{A_{21}}{B_{21}}\frac{kT}{h\nu}$$

Ratio of Einstein coefficients

$$\frac{A_{21\ \text{spontaneous}}}{B_{21\ \text{stimulated}}} = \frac{8\pi h\nu^3}{c^3} \quad \text{... (8)}$$

Ratio of spontaneous to stimulated emission rate

$$\frac{A_{21}}{u(\nu)B_{21}} = \left(e^{\frac{h\nu}{kT}} - 1\right) \quad \text{... (9)}$$

Requirement of Lasing action.

1. **Population inversion** $N_2 >> N_1$ or $N_2 >> \frac{N}{2}$ In terms of total atoms N

———— N_2

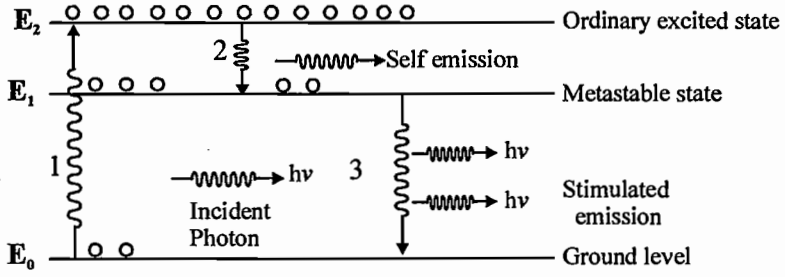
———— N_1 $\qquad N = N_1 + N_2$ Threshold condition $N_2 \simeq \frac{N}{2}$

$$\frac{N_2}{N_1} = e^{-(E_2 - E_1)/kT}$$

It is difficult to have large number of atoms in the excited state.

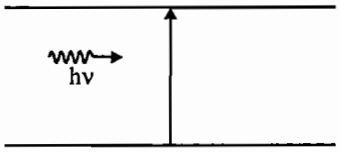
Pumping of atoms from lower to higher state is needed.

2. **Optical Pumping:** Let E_0 be the ground energy state of an atom and the two excited states are E_1 and E_2 respectively. Now if light is made incident by a flash tube, many atoms absorb photons corresponding to the energy $(E_2–E_0)$ and get excited to the energy state E_2 as shown by the transition 1 in figure. These excited atoms after nearly $10^{-8}s$ emit photons of energy $(E_2–E_1)$ by self emission and come to the ground energy state as shown by the transition 2 in figure. If the energy state E_1 is the metastable state, then it is not possible for the atom to come to the ground energy state E_0 by the self emission, but it is possible for the atom to come from the metastable energy state E_1 to the ground energy state E_0 only by the stimulated emission. Thus, the number of atoms in the energy state E_1 is very much increased in comparision to those in the ground state E_0. This is called the population inversion.



Excitation of atoms from ground to excited state by the means of optical radiations.

We cannot achieve lasing action in a two level system. We cannot have a 2-level laser.

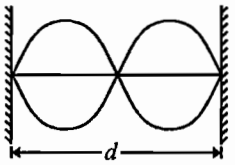


3. **Optical Cavity** is needed to amplify the power level of laser-beam. This optical cavity is made from 2 mirrors, out of which one is completely reflecting and another is partially reflecting. The distance between 2 mirrors is adjusted such that reflected-wave suffers a phase change of π (180°) and in the round trip total phase changed is 2π.

If d = length of the cavity = distance between 2 mirrors

$$\text{Phase difference} = \frac{2\pi}{\lambda} \times \text{Path difference}$$

$$2m\pi = \frac{2\pi}{\lambda} \times 2d, \qquad \text{No. of nodes} \equiv m = 0, 1, 2, 3, ...$$



$$\boxed{d = \frac{m\lambda}{2}}$$ d = Integer multiple of half wavelength

If refractive index of medium inside cavity = n_0,
Wavelength of electromagnetic wave inside the cavity.

$$\lambda = \frac{\lambda_0}{n_0} \qquad \lambda_0 \rightarrow \text{free space wavelength (frequency unchanged)}$$

$$\nu = \frac{c}{\lambda_0} = \frac{v}{\lambda}, \quad \boxed{d = \frac{m\lambda}{2} = \frac{m\lambda_0}{2n_0}} = \frac{mc}{2n_0\nu}$$

Frequency of the wave inside the cavity

$$\boxed{\nu = \frac{2n_0 d}{mc}} = \frac{mc}{2n_0 d}$$

Mode Separation: Frequency difference between two successive modes $m + 1$, m

$$\Delta\nu = \frac{c}{2n_0 d}[m+1-m], \quad \boxed{\Delta\nu = \frac{c}{2n_0 d}} = \boxed{\frac{v}{2d}}$$

Speed of EM wave in medium $v = \frac{c}{n_0}$

Time taken by EM wave in a round trip

$$\boxed{t = \frac{2d}{v} = \frac{2dn_0}{c}}$$

Minimum pumping power per unit volume to maintain the population inversion.

$$\boxed{P = \frac{N_2 h\nu_p}{t_{sp}}}$$, N_2 = No. of atoms in excited state (per unit volume)

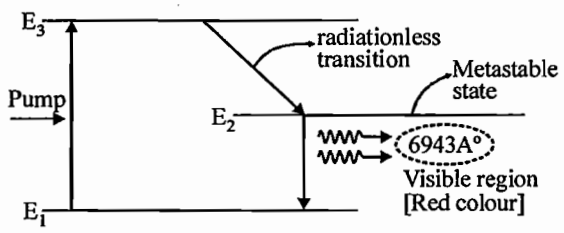
ν_p = Average pumping frequency, t_{sp} = Life-time of spontaneous decay
N = Total no. of atoms per unit volume

$$\boxed{P_{\text{min, threshold}} \cong \frac{N}{2}\frac{h\nu_p}{t_{sp}}}$$

Different types of lasers

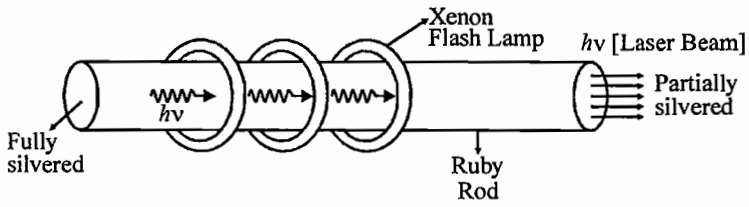
(i) **Ruby Laser [Cr : Al_2O_3] :** Cr doped Al_2O_3 laser Ruby Laser is a 3 level laser and it is solid state laser. In Ruby-laser, Ruby consist of Cr^{3+} to provide red colour ions doped into crystalline Al_2O_3 with some of the Al^{3+} ions replaced by Cr^{3+} ions.

Cr ions in the ground state can absorb a photon of 5500A° under optical pumping.



This optical pumping is done by Xenon-flash lamp.

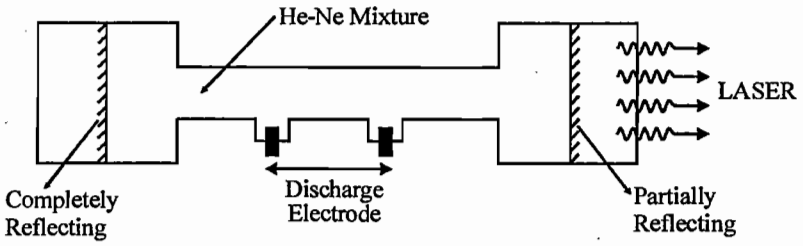
Ruby laser is not tunable laser.



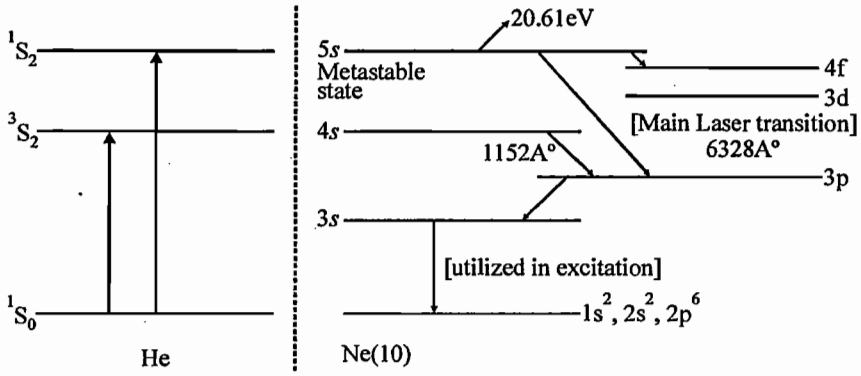
(ii) **Helium - Neon Laser** is Gas-laser and it is 4-levels laser. In this mixture of He and Ne gas in ratio of 10 : 1 (or 7 : 1) placed inside the discharge tube at a pressure of 1 Torr.

Laser transition takes place in Neon, the work of He here is to provide the energy to Ne atoms through collision.

Helium help in population inversion

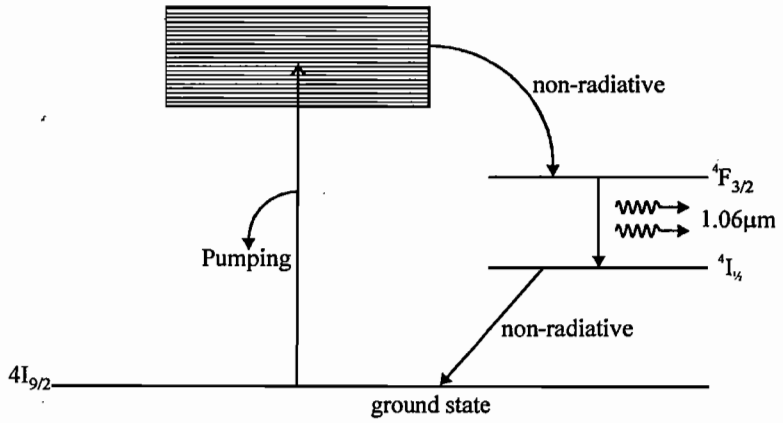


Output power of He-Ne laser few milli watt. This is not a tunable laser [Also Ruby Laser]
[$1e^-$ excite at one time out of $1s^2$]



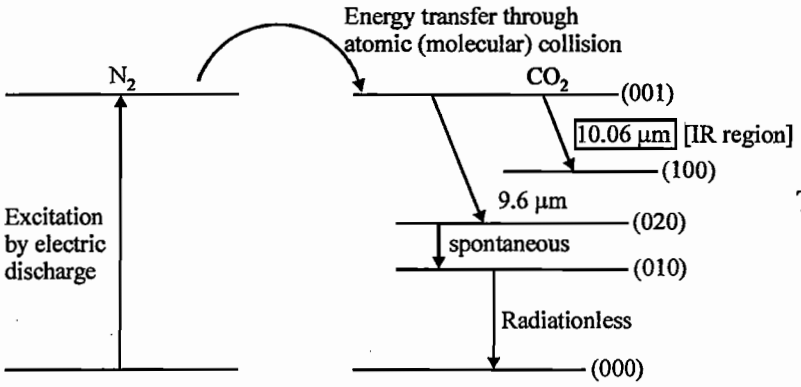
5s → 4p
5s → 3p (6328 A°)
4s → 3p
3p → 3s (spontaneous transition)
3s → ground state (Radiationless) → Energy in form of heat.
Narrow tube ⇒ Pressure increases ⇒ Collision more frequent
Spontaneous transition ⇒ Incoherent radiation

(iii) **Nd : YAG LASER (Nd : $Y_3Al_5O_{12}$).** This is a solid state Laser in which $Y_3Al_5O_{12}$ (YAG) crystal is doped with Nd^{3+} ions [Neodymium].
In this electrons are excited to pump bands by absorption of photons from a flash lamp. Its main Laser transition occurs between $\boxed{^4F_{3/2} \rightarrow {}^4I_{1/2}}$ states. It lies in near infrared region with wavelength $\boxed{1.06\mu m}$.
This is a 4-level laser. This is used for pumping in tunable lasers. It can give a power of 20-30 watt.



(iv) **CO_2 LASER** is a molecular laser. Energy-levels are quantised in vibrational and rotational levels. Active medium for CO_2 Laser is

$CO_2 : N_2 : He \equiv 1 : 4 : 5$



CO_2 is not a tunable laser. It is 5 level laser. Lasing action taking place between vibrational states.

(v) **He - Cd ≡ He - Ne** : Active lasing-medium is Cadmium.

2 Transitions → 442 nm [Blue]
2 Transitions → and other in UV

(vi) **Semi-Conductor Laser** is a p-n junction between direct band-gap semiconductor like GaAs.

Wavelength of Laser Light $\boxed{\lambda = \frac{hc}{E_g} = \frac{1242}{E_g\,(in eV)}}$ nm, where E_g is the band gap energy.

It is solid state laser and tunable laser.
If GaAs is doped with Aluminium or phosphorous, its band-gap can be changed, hence λ of lasing light can be changed.

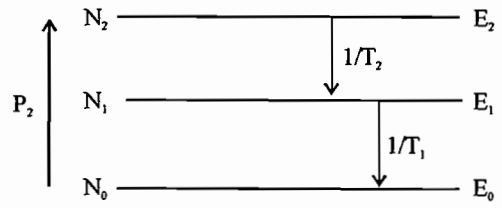
(vii) **Dye-Laser** can be constructed using an organic substance dissolved in water or methanol and this is a tunable laser.

Prob. In atomic system shown in the figure, the pump P2 excites atoms from state 0 to state 2 at rate of 10^{20} atoms/cm^3–sec. Assume that

(i) State 0 is never depleted, $\frac{dN_D}{dt} = 0$

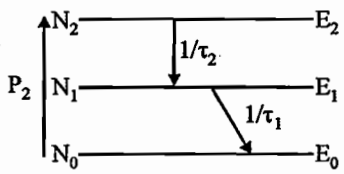
(ii) Initial population densities N_1 and N_2 are two zero.

(iii) Allowed decay rates with $T_2 = 1\,\mu_s$, $T_2 = 2\,\mu_s$ and neglect stimulated emission.



(a) Write the rate execution for states (ii) and (i)
(b) Obtain the solutions for N_2CH and N_1CH.
(c) Steady state populations of state (ii) and (i).

Soln.(a)



Pumping (Absorption) is always stimulated.

$$\frac{dN_2}{dt} = -B_{21}N_2u(\nu) \quad \text{... (1)}$$

$$\frac{dN_2}{dt} = -A_{21}N_2 \quad \text{... (2)}$$

$$= -\frac{N_2}{\tau_{21}} \quad \text{... (3)} \qquad \left[\because A_{21} = \frac{1}{\tau_{21}}\right]$$

By $u(\nu) = \frac{\sigma I}{h\nu}$ ... (4)

σ = cross sectional area, I = Intensity, ν = Frequency

From equation (1) and (4) $\frac{dN_2}{dt} = -\frac{\sigma_{emission} I}{h\nu_2}N_2 - \frac{N_2}{\tau_{21}} + \frac{\sigma_{absorption} I N_o}{h\nu_0}$

Coming to level +ve, going far away from level –ve

$$\frac{dN_1}{dt} = +\frac{\sigma_{emission} I}{h\nu_2}N_2 + \frac{N_2}{\tau_{21}} - \frac{\sigma_{emission} I N_1}{h\nu_1} - \frac{N_0}{I_{10}}$$

$$\frac{dN_2}{dt} = P_2 - \frac{N_2}{\tau_2} \quad \text{... (1)}$$

$$\frac{dN_1}{dt} = \frac{N_2}{\tau_2} - \frac{N_1}{\tau_1} \quad \text{... (2)}$$

(b) $N_2(t) = ?$, $N_1(t) = ?$, $N_1(0) = 0$, $N_2(0) = 0$

from (1) $\frac{dN_2(t)}{dt} = P_2 - \frac{N_2}{\tau_2}$ Let $P_2 - \frac{N_2}{\tau_2} = u$ $-dN_2 = \tau_2 du$

$-I_2\frac{du}{u} = dt$, $\ln u = \frac{-t}{\tau_2} + C$, At $t = 0$, $N_2(0) = 0$

$\ln[P_2 - 0] = 0 + C \Rightarrow C = \ln P_2$

$$\ln\left[1 - \frac{N_2(t)}{P_2\tau_2}\right] = -\frac{t}{\tau_2}, \quad 1 - \frac{N_2(t)}{P_2\tau_2} = e^{-t/\tau_2}$$

$$\boxed{N_2(t) = (1 - e^{-t/\tau_2})P_2\tau_2}$$

From (2) $\frac{N_2}{\tau_2} - \frac{N_1}{\tau_1} = v$, $\ln v = -\frac{t}{\tau_1} + C$, $\ln\left[\frac{N_2}{\tau_2} - \frac{N_1}{\tau_1}\right] = -\frac{t}{\tau_1} + C$, C = 0

$$\frac{N_2}{\tau_2} - \frac{N_1}{\tau_1} = e^{-t/\tau_1}, \quad N_1 = \tau_1\left[\frac{N_2(t)}{\tau_2} - e^{-t/\tau_1}\right]$$

(c) Steady state → Flow same

$$\frac{dN_1}{dt} = 0 \quad \text{.....(1)}, \qquad \frac{dN_2}{dt} = 0 \quad \text{..... (2)}$$

$N_2 = P_2\tau_2, \quad N_2\tau_1 = N_1\tau_2$

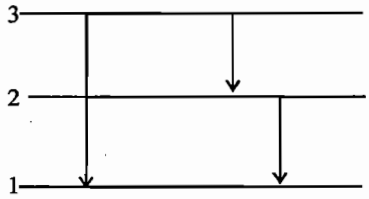
$N_2 = 10^{20} \times 10^{-6}$ atoms / m^3-sec $= 10^{14}$ atoms / m^3 – sec

Prob. The figure shows the energy levels of 3 level atomic system with Einstein A coefficient $A_{32} = 7\times10^7\ sec^{-1}$, $A_{31} = 1\times10^7\ sec^{-1}$, $A_{21} = 1\times10^8\ sec^{-1}$.

(a) Can the system be used for ..... action between the levels 2 and 1?

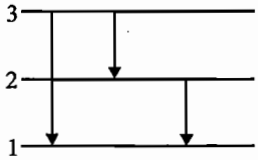
(b) What is the lifetime of level 3.

(c) At the time t = 0, N atoms/cm^3 are excited and the level 3 by some external mechanism, find the rate of change of population of the state 3.



Soln.(a) $A_{32} = 7 \times 10^7\ sec^{-1}$, $A_{31} = 1 \times 10^7\ sec^{-1}$, $A_{21} = 10^8\ sec^{-1}$, $\tau_2 = \dfrac{1}{10^8}$ sec

No Lasing action because this is a very low line state.



(b) Life-Time of level 3

$$\frac{1}{\tau_3} = \frac{1}{\tau_{32}} + \frac{1}{\tau_{31}} \qquad \text{... (1) (Transition from level } 3 \to 2)$$

$$\because\ \tau_{32} = \frac{1}{A_{32}},\ \tau_{31} = \frac{1}{A_{31}} \qquad \text{... (2)}$$

$$\tau_3 = \frac{1}{A_{32} + A_{31}} = \frac{1}{8}\times10^{-7}\ \text{sec} = \boxed{1.25\times10^{-8}\ \text{sec}}$$

(c) Transition $3 \to 1$ and $3 \to 2$ are spontaneous

$$\frac{dN_3}{dt} = -\frac{N_3}{\tau_{31}} - \frac{N_3}{\tau_{32}}$$

Condition $t = 0$, $N_3(0) = N$, $\dfrac{dN_3}{dt} = -N_3\left[\dfrac{1}{\tau_{31}} + \dfrac{1}{\tau_{32}}\right]$

$$\frac{dN_3}{N_3} = -\frac{1}{\tau_3}dt, \quad \ln N_3 = -\frac{t}{\tau_3} + C \Rightarrow C = \ln N$$

$$\boxed{N_3(t) = Ne^{-t/\tau_3}}$$

Prob. The level structure shown in the figure is for an Erbium-doped glass laser. The transition rates can be expressed in terms of emission cross-section σ_e and the absorption coefficient σ_a as $\dfrac{dN}{dt} = \dfrac{\sigma I}{h\gamma}N$. Where I and γ are

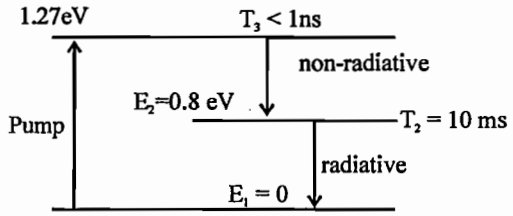
intensity and frequency of corresponding transition.

(i) What are the wavelengths λ_p and λ_s of the optical pump and signal respectively.

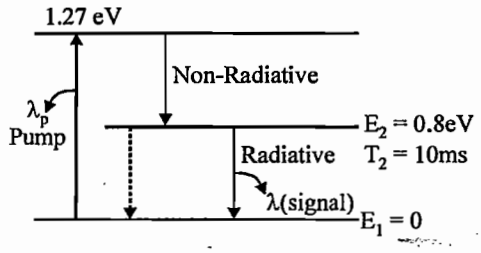
(ii) If N_1 and N_2 are population densities of states having energies E_1 and E_2 respectively, write rate equations in terms of $\sigma_e(\lambda_s)$, $\sigma_a(\lambda_s)$ and $\sigma_a(\lambda_p)$.

(iii) Show that under steady state conditions

$$\frac{N_1}{N_2} = \frac{\frac{\sigma_e(\lambda_s)I_s}{h\nu_s} + \frac{1}{I_2}}{\frac{\sigma_a(\lambda_s)I_s}{h\nu_s} + \frac{\sigma_a(\lambda_p)I_p}{h\nu_p}}$$



Soln.(i) $\lambda_p = \frac{1240}{1.27\,eV}$ nm, $\lambda_s = \frac{1240}{0.8\,eV}$ nm



(ii) Reaching N_3 by stimulated absorption

$$\frac{dN_2}{dt} = \underset{\substack{\downarrow \\ \text{stimulated absorption}}}{\frac{\sigma_a(\lambda_p)I_pN_1}{h\nu_p}} - \underset{\substack{\downarrow \\ \text{stimulated emssion}}}{\frac{\sigma_e(\lambda_s)I_sN_2}{h\nu_s}} - \frac{N_2}{\tau_2} + \frac{\sigma_a(\lambda_s)I_sN_1}{h\nu_s} \quad \ldots (1)$$

$$\frac{dN_1}{dt} = -\frac{\sigma_a(\lambda_p)I_pN_1}{h\nu_p} + \frac{\sigma_e(\lambda_s)I_sN_2}{h\nu_s} + \frac{N_2}{T_2} - \frac{\sigma_a(\lambda_s)I_sN_1}{h\nu_s} \quad \ldots (2)$$

(iii) $\frac{dN_1}{dt} = 0 = \frac{dN_2}{dt}$ (steady state)

$$N_1\left[\frac{\sigma_a(\lambda_s)I_s}{h\nu_s} + \frac{\sigma_a(\lambda_p)I_p}{h\nu_p}\right] = N_2\left[\frac{\sigma_e(\lambda_s)I_s}{h\nu_s} + \frac{1}{\tau_2}\right]$$

$$\frac{N_1}{N_2} = \frac{\left[\frac{\sigma_e(\lambda_s)I_s}{h\nu_s} + \frac{1}{\tau_2}\right]}{\left[\frac{\sigma_a(\lambda_s)I_s}{h\nu_s} + \frac{\sigma_a(\lambda_p)I_p}{h\nu_p}\right]}$$

Prob. Find $\frac{A}{B}$ ratio at room temperature for two levels with energy difference of 10.2 eV.

Soln. $\frac{A}{B} = \frac{8\pi h\nu^3}{c^3} \frac{J\,\text{sec}\,\text{sec}^{-3}}{m^3\,\text{sec}^{-3}}$ $E = h\nu \Rightarrow \nu = \frac{10.2}{h}$

$$\frac{A}{B} = \frac{8\times3.14\times6.6\times10^{-34}\times(10.2)^3\times1.6^3\times10^{-57}}{(3\times10^8)^3\times(6.6\times10^{-34})^3}$$

$$B \rightarrow \frac{m^3}{J-\sec^2}, \quad A \rightarrow \sec^{-1}$$

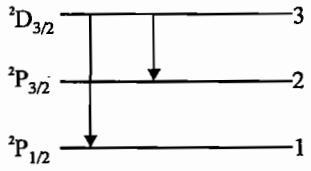
Prob. Calculate the relative rate of spontaneous and stimulated process in the microwave region ($\nu = 10^{10}$ Hz at 300K).

Soln. $$\frac{NA}{NBu(\nu)} = \frac{\text{rate of spontaneous}}{\text{rate of stimulated}}$$

$$\frac{A}{Bu(\nu)} = (e^{h\nu/kT} - 1) = \left(\frac{\frac{6.6\times10^{-34}\times10^{10}}{}}{e^{1.38\times10^{-23}\times300} - 1} \right)$$

Prob. In He-Cd LASER, transitions take place between $^2P_{3/2}$ and $^2D_{3/2}$ and $^2P_{1/2}$ with wave-lengths 353.6 and 325nm. $^2D_{3/2} \xrightarrow{353.6nm} {}^2P_{3/2}$ and $^2D_{3/2} \xrightarrow{325\ nm} {}^2P_{½}$. The relative prob of radiative transmission are 1.6×10^5 $\sec^{-1}$ and 7.5×10^5 $\sec^{-1}$ respectively.

Soln. $A_{31} = 7.5 \times 10^5$ $\sec^{-1}$, $A_{32} = 1.6 \times 10^5$ $\sec^{-1}$



Life Time of $^2D_{3/2} = \tau_3$ = level-3 life time

$$\frac{1}{\tau_3} = (7.5 \times 10^5 + 1.6 \times 10^5) = 9.1 \times 10^5 \sec^{-1}, \quad \tau_3 = \frac{1}{9.1\times10^5} \sec$$

Prob. Calculate the doppler half-intensity breadth of sodium D-lines at 5893 Å corresponding to temperatures of 500K. R = 8.31×10^7 erg/mole, C = 3×10^{10} cm/sec atomic weight = 22.99 gm/mole.

Soln. $$\Delta\nu_D = 1.67 \ \frac{\nu_0}{C}\sqrt{\frac{2k_BT}{M}} \text{ Hz}$$

$$\nu = \frac{C}{\lambda} \Rightarrow \Delta\nu = -\frac{C}{\lambda^2}\Delta\lambda, \quad \Delta\nu = -\frac{C}{\lambda}\frac{\Delta\lambda}{\lambda} \Rightarrow \frac{\Delta\nu}{\nu} = -\frac{\Delta\lambda}{\lambda}$$

$$\Delta\nu_D = 7.16 \times 10^{-7} \ \nu_0\sqrt{\frac{T}{m}} \text{ htz, } T \rightarrow \text{Kelvin, } m \rightarrow \text{amu}$$

$$\Delta\nu_D = 7.16 \times 10^{-7} \ \lambda_0\sqrt{\frac{T}{M}}$$

$$\Delta\nu_D = 7.16 \times 10^{-7} \times 5893 \times 10^{-10} \sqrt{\frac{500}{23}}, \quad \text{sodium D-lines at 5893 A°.}$$

$= 1.96 \times 10^{-12}$ m, $= 0.0196$A°, $= 0.02$ A°.

Prob. The ionization energy of lithium is 5.39 eV. Use this figure to find the effective charge that acts on the outer (2λ) electron of the lithium atom.

Soln. $Li \rightarrow 2s \rightarrow n = 2$ state

$$E_{Li} = \frac{Zn^2 E_H}{n^2}, \quad 5.39 \text{ eV} = \frac{Zn^2 \times 13.6eV}{4}, \quad Zn = 2\sqrt{\frac{5.39}{13.6}} = 1.26$$

Effective nuclear charge Zn e = 1.26e

Prob. Given effective nuclear charge, Find ionization energy.

Soln. $E_{Li} = \frac{Zn^2 E_H}{4}$

Prob. Estimate the electric field needed to pull an electron out of an atom in a time comparable to that for the electron to go around the nucleus.

Soln. H, Li^{2+}, He^{+} (having different radii). Energy of e^- moving around the nucleus = eEa orbit radius.

$$a = \frac{a_0}{z},$$

$e E a \geq$ B.E. $= z^2 E_H = z^3 \times 13.6$ eV [for emitting e^-]

$$E \simeq \frac{13.6\, z^3}{0.53 \times 10^{-10}} \text{ V/m} \simeq 2.5 \times 10^{11}\, z^3 \text{ V/m}$$

$E_H \simeq 2.5 \times 10^{11}$, $E_{He^+} \simeq 8 \times 2.5 \times 10^{11} = 20 \times 10^{11}$ V/m, $E_{Li^{2+}} \simeq 27 \times 2.5 \times 10^{11}$ V/m

Prob. An electronic transition in ions of ^{12}C leads to photon emission near $\lambda = 500$ nm ($h\nu = 2.5$ eV). The ions are in thermal equilibrium at an ion temperature $kT = 20$ eV, a density $n = 10^{24}\, m^{-3}$, and a non-uniform magnetic field which ranges up to B = 1 Tesla.

(a) Briefly discuss broadening mechanisms which might cause the transition to have an observed width $\Delta\lambda$ greater than that obtained for very small values of T, n and B.

(b) For one of these mechanisms calculate the broadened width $\Delta\lambda$ using order-of-magnitude estimates of needed parameters.

Soln.(b) $\Delta\nu_N = \frac{1}{2\pi\tau} = \frac{1}{2 \times 3.14 \times 10^{-8}}$ Hz

$$\Delta\nu_D = 1.67 \frac{\nu}{C}\sqrt{\frac{2kT}{M}} = 1.67 \times \frac{1}{\lambda}\sqrt{\frac{20 \times 2 \times 1.6 \times 10^{-19}}{12/6.02 \times 10^{26}}} = 6 \times 10^{10} \text{ Hz}$$

$$\Delta\nu_C = \frac{1}{2} nd^2 \sqrt{\frac{3kT}{M}} = \frac{1}{2} \times 10^{24} \times 2 \times 2 \times 10^{-10} \times (0.5)^2 \sqrt{\frac{3 \times 20 \times 1.6 \times 10^{-19}}{12 \times 1.67 \times 10^{-27}}}$$

$\simeq 0.5 \times 10^8 \times 2 \simeq 10^8$ Hz

Wave No. $\Delta\bar{\nu}_D = \frac{\Delta\nu_D}{C} m^{-1} = 2 \times 10^{+2}\ m^{-1} = 2\ cm^{-1}$

$$\Delta\bar{\nu}_N = \frac{\Delta\nu_N}{C} m^{-1} = \frac{1}{2 \times 3 \times 3.14} = 0.05\ m^{-1}$$

$= 0.0005\ cm^{-1} = 5 \times 10^{-4}\ cm^{-1}$

Natural Broading does not depend upon temperature or pressure.

$$\Delta\bar{\nu}_C = \frac{1}{2}\frac{nd^2}{C}\sqrt{\frac{3kT}{M}} = \frac{10^8}{3 \times 10^8} = \frac{1}{3} = 0.333\text{m} = 3.33 \times 10^{-3} \text{ cm}$$

Hence, Doppler broadening > Collision broadening > Natural broadening

Prob. Estimate (order of magnitude) the Doppler width of an emission line of wavelength $\lambda = 5000\text{Å}$ emitted by argon A = 40, Z = 18, at T = 300 K.

Soln. $\Delta\lambda_D = 7.16 \times 10^{-7} \times 5000 \times 10^{-10}\sqrt{\frac{300}{40}}$

$= 35.80 \times 10^{-14}\sqrt{7.5}$
$= 98.04 \times 10^{-14}\text{m}$
$= 9.8 \times 10^{-3}\ \text{A}^\circ$
$= 0.98 \times 10^{-3}\ \text{nm}$
$\simeq 1.4 \times 10^{-3}\ \text{nm}$

Prob. Hyperfine splitting in hydrogen ground state is 10^{-7}, 10^{-5}, 10^{-3}, 10^{-1} eV.

Soln. Hyperfine splitting in hydrogen ground state is 10^{-5} eV.

Prob. The hyperfine structure of hydrogen
(a) is too small to be detected.
(b) arises from nuclear spin.
(c) arises from finite nuclear size.

Soln. Hyperfine structure of hydrogen arises from nuclear spin.

Prob. Spin-orbit splitting of the hydrogen $2p$ state is 10^{-6}, 10^{-4}, 10^{-2}, 10^{0} eV.

Soln. Spin-orbit splitting of H_2 $2p$ state is 10^{-4} eV

Prob. The ground state of hydrogen atom is $1s$. when examined very closely, it is found that the level is split into two levels.
(a) Example why this splitting takes place.
(b) Estimate numerically the energy difference these two levels.

Soln.(a) $\because$ Nuclear spin of H is $\frac{1}{2}$, $1S \rightarrow {}^2S_{½}$

$F = |I - J|$ to $|I + J| = 0, 1$
Therefore, s will split due to hyperfine-splitting

(b) $\begin{matrix} F=1 \\ F=0 \end{matrix}$ $\Delta E_{\text{Hyperfine}} \equiv A\ \vec{I}\,.\,\vec{J} \simeq 10^{-5}$ eV

$\Delta E_{\text{Fine}} \equiv A\ \vec{L}\,.\,\vec{S} \simeq 10^{-4}$ eV

Prob. Calculate to an order of magnitude, the following properties of the 2p-1s electromagnetic transition in an atom formed by a muon and a strontium nucleus (Z = 38):
(a) the natural line width. (Hint: the lifetime of the 2p state of hydrogen is 10^{-9} sec)

Soln. $\Delta\nu_N = \frac{1}{2\pi\tau_\mu}$

Life time of μ will be $\frac{\tau_\mu}{\tau_H} = \frac{1}{Z^4}\frac{m_e}{m_\mu}$, $m_\mu = 207m_{c,}$ $\tau_\mu = \frac{9.1\times10^{-31}kg}{(38)^4 \times 207me} = 2.4 \times 10^{-18}$ sec

$\Delta\nu_N = 6.6 \times 10^{16}$ Hz

Prob. The moun is a relatively long-lived elementary particle with mass 207 times the mass of electron. The electric charge and all known interactions of the muon are identical to those of the electron. A "muonic atom" consists of a neutral atom in which one electron is replaced by a muon.

(a) What is the binding energy if the ground state if muonic hydrogen ?

(b) What ordinary chemical element does muonic lithium (Z=3) resemble must ? Explain your answer.

Soln.(a) $E_H = 13.6eV$, $E \propto R_\infty$, $R \propto \mu$, $\mu_\mu = 207\mu_H$

$R_\mu = 207R_H$, $E_\mu = 207E_H$, $E_\mu = 2.82\times10^{+3}eV$

(b) Munonic Lithium resembles with He, CO_3, μ and e^- are two different fernions. Hence μ will remain in its ground state and $2e^-$ and remain in their ground state. Hence it behaves as He (Helium).

Prob. List the ground-state configurations and the lowest-energy terms of the following atoms: He, Li, Be, B, C, N, O, F and A.

Soln.

He	$^1S_0$
Li	$^2S_{½}$
Be	$^1S_0$
B	$^2P_{½}$
C	$^3P_0$
N	$^4S_{3/2}$
O	$^3P_2$
F	$^2P_{3/2}$
Ne	$^1S_0$
Ar	$^1S_0$

Prob. Answer each of the following questions with a brief, and where possible quantitative statement. Given your reasoning.

(a) A beam of neutral atoms passes through a Stern-Gerlach apparatus. Five equally spaced lines are observed. What is the total angular momentum of the atom ?

(b) What is the magnetic moment of an atom in the state $^3P_0$? (Disregard nuclear effects)

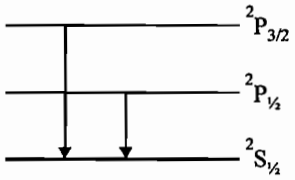
(c) In a hydrogen gas discharge both the spectral lines corresponding to the transitions $2^2P_{1/2} \rightarrow 1^2S_{1/2}$ and $2^2P_{3/2} \rightarrow 1^2S_{1/2}$ are observed. Estimate the ratio of their intensities.

Soln.(a) 2J + 1 = 5, J = 2 ground state of silver atom $^2S_{½}$

(b) $^3P_0$, magnetic moment $|\vec{\mu}_J| = g\sqrt{J(J+1)}$, $\mu_B = 0$, $\because$ J = 0

(c) $2\ ^2P_{1/2} \rightarrow 1\ ^2S_{1/2}$ and $2\ ^2P_{3/2} \rightarrow 1\ ^2S_{1/2}$

$\frac{I_1}{I_2} = \frac{4}{2} = 2$ and J + 1



Prob. Apply the Russell-Saunders coupling scheme to obtain all the states associated with the electron configuration $(1s)^2(2s)^5(3p)$. Label each states by the spectroscopic notation of the angular-momentum quantum numbers appropriate to the Russell-Saunders coupling.

Soln. $1s^2, 2s^2, 2p^5, 3p$ (2^{nd} excited state of Neon)

$2p^6 \rightarrow 3p$

$1s^2, 2s^2, 2p^6$ [Neon]

Complimentary states of $2p^5$ are $2p^1, 3p^1$

$v_1 = 1, l_2 = 1$, L = 0, 1, 2, S = 0, 1

$J = 0, 1, 2$ [$S = 0, J = 0, 1, 2$]
$J = 1$ [$S = 1, L = 0$]
$J = 0, 1, 2$ [$S = 1, L = 1$]
$J = 1, 2, 3$ [$S = 1, L = 2$]
$\rightarrow {}^1S_0, {}^1P_1, {}^1D_2$
$\rightarrow {}^3S_1, {}^3P_0, {}^3P_1, {}^3P_2$
$\rightarrow {}^3D_1, {}^3D_2, {}^3D_3$
$2p^5$ > half filled hence ground state is ${}^3D_3$

Prob. The ground configuration of Sd (scandium) is $1s^2 2s^2 2p^6 3s^2 3p^6 3d 4s^2$
(a) To what term does this configuration give rise ?
(b) What is the appropriate spectroscopic notation for the multiplet levels belonging to this term ? What is the ordering of the levels as a function of the energy ?
(c) The two lowest (if there are more than two) levels of this ground multiplet are separated by 168 cm^{-1}. What are their relative population at T = 2000 K ?

$h = 6.6\times10^{-34}$ J sec, $c = 3\times10^{8}$ m/s, $k = 1.4\times10^{-23}$ J/K.

Soln. $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, \boxed{3d^1}, 4s^2$
(a) $3d \rightarrow {}^2D_{5/2}, {}^2D_{3/2}$
(b) ${}^2D_{3/2}$ then ${}^2D_{5/2}$ $\because$ Energy of a ${}^2D_{3/2}$ < Energy of ${}^2D_{5/2}$

(c)
(2) ——— ${}^2D_{5/2}$
168 cm^{-1}
(1) ——— ${}^2D_{3/2}$

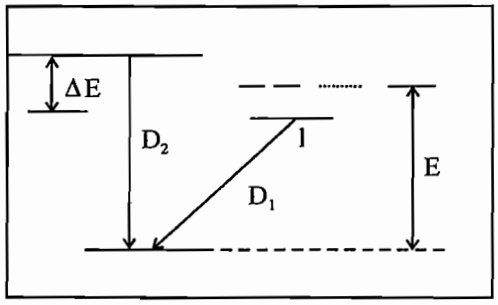
$$\frac{N_2}{N_1} = \frac{g_2}{g_1}\, e^{-\frac{(E_2-E_1)}{kT}}$$

$g \rightarrow$ degeneracy $g_1 = 2J_1 + 1$, $g_2 = 2J_2 + 1$
$\Delta E = E_2 - E_1 = 1.68 \times 10^4 \times 6.6 \times 10^{-34} \times 3 \times 10^8$ joule

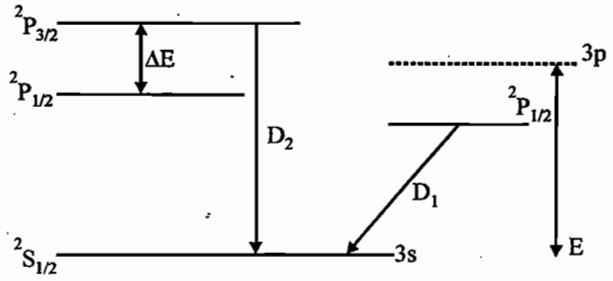
$$\Delta E = \frac{1}{8066}\times 168 \text{ eV} =$$

At 2000K $N_2 > N_1$, $\frac{N_2}{N_1} = 1.17$

Prob. For the sodium doublet give:
(a) Spectroscopic notation for the energy levels in the figure.
(b) Physical reason for the energy difference E.
(c) Physical reason for the splitting ΔE.
(d) The expected intensity ratio D_2 / D_1 if $kT >> \Delta E$.



Soln. Different $l \rightarrow$ different path $n \rightarrow l \rightarrow$ L – S. Difference between 3p and 3s is due to l.



Reason of ΔE is spin-orbit interaction $\frac{I_{D_2}}{I_{D_1}} = \frac{2}{1}$.

Prob. For each of the following atomic radiative transitions, indicate whether the transition is allowed or forbidden under the electric-dipole radiation selection rules. For the forbidden transitions, cite the selection rules which are violated.

(a) He: $(1s)(1p)\ ^1P_1 \rightarrow (1s)^2\ ^1S_0$

(b) C: $(1s)^2(2s)^2(2p)(3s)\ ^3P_1 \rightarrow (1s)^2(2s)^2(2p)^2\ ^3P_0$

(c) C: $(1s)^2(2s)^2(2p)(3s)\ ^3P_0 \rightarrow (1s)^2(2s)^2(2p)^2\ ^3P_0$

(d) Na: $(1s)^2(2s)^2(2p)^6(4d)\ ^2D_{5/2} \rightarrow (1s)^2(2s)^2(2p)^6(3p)\ ^2P_{1/2}$

(e) He: $(1s)(2p)\ ^3P_1 \rightarrow (1s)^2\ ^1S_0$

Soln. 1 – electron, $\Delta l = \pm 1$, $\Delta J = 0, \pm 1$

Many electrons $\Delta L = 0, \pm 1$, $\Delta S = 0$, $\Delta J = 0, \pm 1$

$J = 0 \not\longleftrightarrow J = 0$

(a) allowed, not allowed (b) Allowed as it is two or more e^- transition

(c) $J = 0 \not\longleftrightarrow J = 0$, not allowed

(d) $\Delta J = \pm 2$, not allowed (e) $\Delta S = +1$, $s_1 = 1$, $s_2 = 0$, not allowed

Prob. For Zn, the X-ray absorption edges have the following values in keV:

K 9.67, L_I 1.21, L_{II} 1.05, L_{III} 1.03.

Determine the wavelength of the K_α line.

If Zn is bombarded by 5-keV electrons, determine

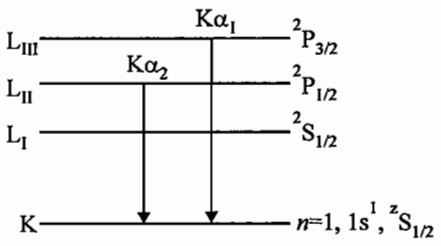
(a) the wavelength of the shortest X-ray line, and

(b) the wavelength of the shortest characteristic X-ray line which can be emitted.

Note: The K level corresponds to $n = 1$, the three L-levels to the different states with $n = 2$. The absorption edges are the lowest energies for which X-rays can be absorbed by ejection of an electron from the corresponding level. The K_α line corresponds to a transition from the lowest L level.

Soln. For one electron transition, $\Delta L = \pm 1$, $\Delta J = 0, \pm 1$,

Multiplicity = 2S + 1 = 2 (S = 1/2)



$K \rightarrow n = 1$, $E_{K\alpha_2} = 9.67 - 1.05 = 8.62$ keV, $E_{K\alpha_1} = 9.67 - 1.03 = 8.64$ keV

$$\lambda_{K_N} = \frac{1242}{8.64\times10^3}\text{ nm} \qquad \lambda_{K\alpha_2} = \frac{1242}{8.62\times10^3}\text{ nm}$$

$K \rightarrow 9.67$ keV, $L_I \rightarrow 1.21$ keV, $L_{II} \rightarrow 1.05$ keV, $L_{III} \rightarrow 1.03$ keV

(a) $\lambda_{min} = \dfrac{hc}{eV} = \dfrac{1242}{5\times10^3}$ nm = 2.48 Å

(b) This bombardment cannot give K_n. K_β(Energy) > Ek_α

Prob. Given a brief description of the Stern-Gerlach experiment answer the following questions:
(a) Why must the magnetic field be in homogeneous? (b) How is the inhomogeneous field obtained?
(c) What kind of pattern would be obtained with a beam of hydrogen atoms in their ground state? Why?
(d) What kind of pattern would be obtained with a beam of mercury atoms (ground state $^1S_0$)? why?

Soln.(a) There must be a force on atomic magnet
(b) By non-symmetric magnetic poles
(c) Two traces obtained. Since, ground state of hydrogen $^2S_{1/2}$, 2J+1=2 H-beam splitted into 2 beams
(d) Hg $\rightarrow$ No splitting $\because$ $^1S_0 \rightarrow 2J + 1 = 1$

Prob. A heated gas of neutral lithium (Z=3) atoms is in a magnetic field. Which of the following states lie lowest. Give brief physical reasons for your answers.
(a) $3\,^2P_{1/2}$ and $2\,^2S_{1/2}$ (b) $5\,^2S_{1/2}$ and $5\,^2P_{1/2}$. (c) $5\,^2P_{3/2}$ and $5\,^2P_{1/2}$ (d) Substates of $5^2P_{3/2}$.

Soln. (a) $2\,^2S_{1/2}$ has lower energy $\because$ $n = 2$

$3\,^2P_{1/2} \rightarrow n = 3$ $\boxed{n \rightarrow \text{effect}}$

(b) $5\,^2S_{1/2}$ and $5\,^2P_{1/2} \Rightarrow 5\,^2S_{1/2}$ $\boxed{l \rightarrow \text{effect}}$
5s 5p

(c) $5\,^2P_{3/2}$ and $5\,^2P_{1/2} \Rightarrow 5\,^2P_{1/2}$ $\boxed{L-S \text{ coupling}}$

(d) Substrate of $5\,^2P_{3/2}$ → +3/2, +1/2, −1/2, −3/2 $\quad M_J = -\dfrac{3}{2}$, $\boxed{\textit{Zeeman Effect}}$

Prob. A particular spectral line corresponding to a J = 1 → J = 0 transition is split in a magnetic field of 1000 gauss into components separated by 0.0016 Å. The zero field line occurs at 1849 Å.
(a) Determine whether the total spin is in the J = 1 state by studying the *g*-factor in the state.
(b) What is the magnetic moment in the excited state?

Soln. J = 1 → J = 0, B = 1 k gauss = 0.1 Tesla
$\Delta\lambda = 1.6 \times 10^{-3}$ Å, $\lambda = 1849$Å
(a) *g*-factor for J = 1, state = ?

J = 1 → M_J: 1, 0, −1; ΔE

$$\Delta E_{M_J} = g\,M_J\,\mu_B B$$
$$\Delta E = g\,\mu_B B = h\Delta\nu \qquad (0,1)$$

$$\nu = \frac{c}{\lambda},\quad \Delta\nu = \frac{c}{\lambda^2}\Delta\lambda,\quad g = \frac{ch\Delta\lambda}{\lambda^2\mu_B B} = \frac{3\times10^8\times6.6\times10^{-34}\times1.6\times10^{-13}}{(1849)^2\times10^{-20}\times9.27\times10^{-24}\times0.1}$$

$$\mu_B = \frac{eh}{4\pi m} = 9.27 \times 10^{-24},\ g = 0.990 = 1$$

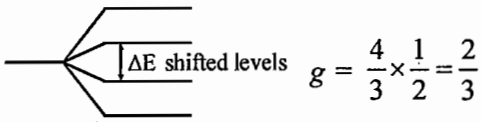
(b) Excited J = 1, magnet moment $|\vec{\mu}_J| = g\sqrt{J(J+1)}\,\mu_B = \sqrt{2}\mu_B$

Prob. The influence of a magnetic field on the spectral structure of the prominent yellow light (in the vicinity of 6000 Å) from excited sodium vapor is being examined (Zeeman effect). The spectrum is observed for light emitted in a direction either along or perpendicular to the magnetic field.

(a) If you have available a spectroscope with a resolution $(\lambda/\delta\lambda)$ of 100000 what magnetic field would be required to resolved clearly the splitting of lines by the magnetic field ? (Numerical estimates to a factor of two or so are sufficient. You may neglect the line broadening in the source.)

Soln. (a) $\frac{\Delta\lambda}{\lambda} = 10^{+5},\ \lambda = 6000\ A^\circ,\ \Delta E = h\Delta\nu = \frac{hc}{\lambda}\frac{\Delta\lambda}{\lambda}$

$= \mu_B B \Rightarrow \Delta E = h\Delta\nu = \frac{hc\Delta\lambda}{\lambda^2} = \mu_B B$



$g = \frac{4}{3}\times\frac{1}{2} = \frac{2}{3}$

B = 0.5 Tesla, B = 10 Tesla

$$\frac{hc}{\lambda^2}\Delta\lambda = \frac{2}{3}\mu_B B$$

Prob. Interatomic forces are due to:

(a) the mutual electrostatic polarization between atoms.

(b) forces between atomic nuclei. (c) exchange of photons between atoms

Soln. (a)

Prob. Which of the following has the smallest energy-level spacing ?

(a) Molecular rotational levels, (b) Molecular vibrational levels, (c) Molecular electronic levels.

Soln. (a)

Prob. Given that the ionisation energies of hydrogen (^{1}H) and Lithium (^{3}Li) are 13.6 eV and 5.39 eV respectively. The effective nuclear charge experienced by the valence electron of ^{3}Li atom may be estimated in terms of the proton charge electron as

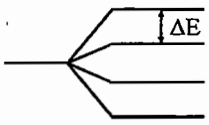
(a) 0.63 e (b) 1.26 e (c) 1.59 e (d) 3.00 e

Soln. (b)

Prob. A sample of a certain element is placed in a magnetic field of flux density 0.3 wb/m^2. How far apart are the Zeeman components of a spectral line of wavelength 4500Å.

Soln. Magnetic field of flux density B = 0.3 Tesla (W/m^2, Weber/m^2 = Tesla)

$\lambda = 4500A^\circ$



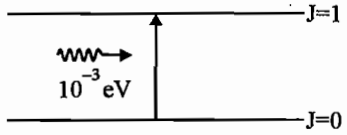
$$\Delta E = h\Delta\nu = \frac{hc}{\lambda^2}\Delta\lambda = \mu_B B,\ \Delta\lambda = \frac{\mu_B B}{hc}\lambda^2 = 2.83 \times 10^{-2} A^\circ$$

Prob. The oxygen molecule O_2 has a bond length 1Å.

(a) On passing photons of energy 10^{-3} eV through oxygen gas they are found to excite the J = 1 rotational estate. Find the moment of inertia of O_2 molecule in units of $\hbar^2$.

(b) O_2 molecule undergo centrifugal stretching at higher rotational angular momenta. As a result the J = 4 to J = 2 transition energy is observed to reduce by 4% as compared to that for rigid roto molecule. What is the bond length of O_2 at J = 4?

Soln. (a) Bond length (r) = 1A°



$\Delta\bar{v}$ = 2B(J + 1) J → lower, $\Delta\bar{v}$ = 2B, $\Delta E = hc\,2B = 10^{-3}$ eV

$$B = \frac{h}{8\pi^2 Ic},\ I = \frac{h^2}{4\pi^2 \times 10^{-3}},\ I = \frac{\hbar^2 \times 10^3}{1.6\times 10^{-19}}.$$

$$I = \frac{100}{1.64}\times 10^{21}\hbar^2,\ I = 6.25 \times 10^{21}\ h^2\ \text{kg-m}^2$$

(b) J = 4 → J = 2 transition

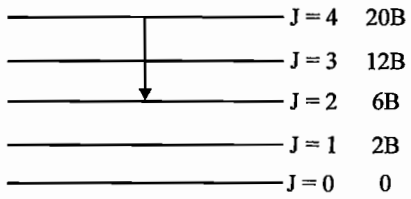
$F_J = BJ(J + 1) - DJ^2(J + 1)^2$

$F_J = BJ(J + 1)$

$F_{J+2} = B(J+2)(J+3)$

$\Delta\bar{v} = B(-J^2 - J + J^2 + 5J + 6) = B(4J + 6)$

$\Delta\bar{v} = B(4\Delta J + 6) = 14B,\ \Delta J = 2$



$\Delta\bar{v}_1 = 14B_1,\ \Delta\bar{v}_2 = 14B_2,\ \frac{\Delta\bar{v}_1}{\Delta\bar{v}_2} = \frac{B_1}{B_2}$ $\qquad B \propto \frac{1}{I}$

$$\frac{\Delta\bar{v}_1}{0.96\Delta\bar{v}_1} = \frac{B_1}{B_2} = \frac{I_2}{I_1},\ I_2 = \frac{I_1}{0.96}$$ ∵ M.I. increases, ∴ Bond length increases $I \propto r^2$

$$I_2 = \frac{I_1}{0.96},\ \mu r_2^2 = \frac{\mu 1A^{\circ 2}}{0.96},\ r_2 = \frac{1A^\circ}{\sqrt{0.96}} = 1.02\text{A}^\circ$$

% change in bond length 2%. ∵ $r \propto \sqrt{I}$, ∴ $\%\Delta I = 4\%$, ($\because \%\Delta r = 2\%$)

Prob. The energy levels of a vibrating diatomic molecule are given by

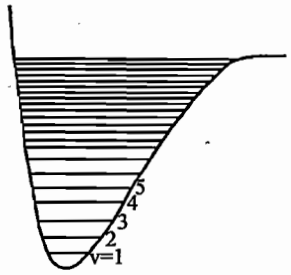
$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega_e - \left(n + \frac{1}{2}\right)^2 x_e\hbar\omega_2$$

where ω_e is the vibration frequency, x_e is the anharmonicity constant and 'n' is vibrational quantum number.

(i) Sketch the vibration energy levels of this molecule.

(ii) If the anharmonicity constant $x_e = 0.001$ to which vibrational state should the molecule be excited for dissociation to occur.

Soln. (i) Anharmonic vibration



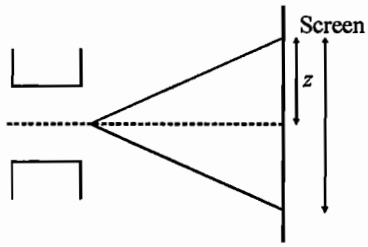
(ii) $X_e = 0.001$, $n = \frac{1}{2X_e} - 1$, $= \frac{1000}{2} - 1 = 499^{th}$ state

Dissociation at 499^{th} vibration level.

Prob. A beam of hydrogen atoms in a Stern-Gerlack experiment obtained from an oven heated to a temperature of 400K passes through a magnetic field of length 1 meter and having a gradient of 10 tesla/m perpendicular to the beam. Calculate the transverse deflection of an atom of the beam at the point where the beam leaves the fidld. The value of the Bohr magneton μ_B is 9.27×10^{-24} A m^2 and the Boltzmann constant k is 1.38×10^{-23} joule/K.

Soln. $\frac{dB_z}{dz} = 10$ Tesla/m

H $\rightarrow$ ground state $^2S_{1/2}$



$g_J = 2$, $m_j = \pm\frac{1}{2}$, $\boxed{z = g_J m_J \frac{\frac{\partial B_z}{\partial z}}{6K_B T} \frac{\mu_B d^2}{T}}$

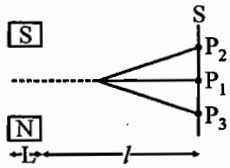
$z = \pm\frac{10\times9.27\times10^{-24}\times1^2}{6\times1.38\times10^{-23}\times400} m$ $\mu_B = 9.27 \times 10^{-24}$,

$k = 1.38 \times 10^{-23}$

$= 0.28$ cm

$2z = 0.56$ cm

Prob. $\frac{\partial B_z}{\partial z}$ = Gradient in magnetic field = 10^3 Tesla/m



Length of pole-piece, L = 0.1m, l = 1m, silver atoms, temperature of over = 600K

Distance between P_2 & P_3?

Soln. $P_1P_2 = g_J M_J \frac{\frac{\partial Bz}{\partial z}\mu_B L\left(\frac{L}{2}+l\right)}{3K_B T}$

$L \equiv d$ in formula $g_J M_J \frac{\frac{\partial Bz}{\partial z}\mu_B d^2}{6kT}$

$P_1P_2 = 0.039$ m, $P_2P_3 = 0.078$ m

speed given (instead of temperature) $\frac{3}{2}kT = \frac{1}{2}mv^2$

m = mass of particular type of atom (kg)

$6k_BT = 2mv^2$ joules

Prob. A narrow beam of neutral particles with spin-½ and magnetic moment is μ is directed along x-axis through a 'Stern-Gerlach' appartus, which splits the beam according to the values of μ_z in the beam. (The apparatus consists essentially of magnets which produce an inhomogeneous gives $B_z(z)$ whose force on the particle moments gives rise to displacements Δz proportional to $\mu_z B_z$).

(a) Describe the pattern of splitting for the cases.

(i) beam polarized along +z-direction. (no splitting)

(ii) beam polarized along +x-direction. (splitted into two parts)

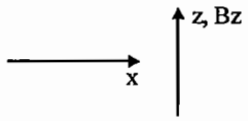
(iii) beam polarized along +y-direction. (splitted into two parts)

(iv) beam unpolarized. (splitted into two parts).

Soln. (a) (*i*) $\tau \rightarrow$ try to change direction of μ_B : μ_B and B are parallel

$\vec{\tau}_M = \vec{m} \times \vec{B}$ (Rotation)

$U = -\vec{m} \cdot \vec{B}$, $\quad \vec{\tau} = \vec{m}_z \times \vec{B}_z = 0$, $\quad \because \vec{\tau} = 0 \Rightarrow$ No splitting

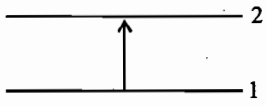


(*ii*) splitting ,

(*iii*) splitting,

(*iv*) splitting in x and y direction

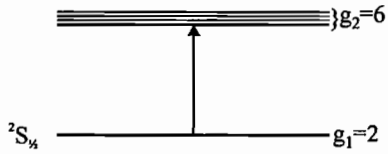
Prob. As shown in the figure light shines on sodium atoms. Estimate the cross-section on resonance for excitation of atoms from the ground state to the first excited state (corresponding to the familiar fellow line). Estimate the width of resonance.



Soln. Sodium D_1 and D_2 lines

Absorption cross-section $\boxed{\sigma_A = \frac{c^2}{2\pi\nu^2}\frac{g_1}{g_2}}$

g = degeneracy



$\lambda = \frac{\lambda_{D_1} + \lambda_{D_2}}{2} = 5893$ $\quad \boxed{\sigma_A = \frac{\lambda^2}{2\pi}\frac{g_1}{g_2}} = 1.84 \times 10^{-14}\ m^2$

Emission cross-section $\boxed{\sigma_E = \frac{\lambda^2}{2\pi}\frac{g_2}{g_1}}$

Prob. The average speed of an electron in first Bohr orbit of an atom of atomic number Z is, in units of the velocity of light,

(a) $Z^{1/2}$ (b) Z (c) Z/137

Soln. (c)

NMR (Nuclear Magnetic Resonance):

In general atomic nuclei have Angular Momentum is given by

$\hbar\sqrt{\ell(\ell+1)}$ with I=0, $\frac{1}{2}$, 1, $\frac{3}{1}$.....

The associated mag. moment.

$$\mu = g\left(\frac{e}{2m_p}\right)\hbar\sqrt{\ell(\ell+1)}$$

Where m_p = mass of proton and g is g-factor.

The mag. moment along the direction of external mag. field B is

$$\mu_z = g\left(\frac{e}{2m_p}\right)M_I\hbar, \qquad g\mu_N M_I, \qquad M_I = I, I-1....-I$$

$$\left(\mu_N = \frac{eh}{2m_p}\right)$$

For $I = \frac{1}{2}, \mu_z = \frac{3}{2}$ of $\mu_N, \frac{1}{2}$ of $\mu_N, \frac{-1}{2}$ of $\mu_N, \frac{-3}{2}$ of μ_N

And magnetic interaction energy

$= -\bar{\mu}.\bar{B}$

$= -\mu B\cos\theta$

$= -(\mu\cos\theta)B$

$= -\mu_z B$

$= \frac{-1}{2}g\mu_N B, \frac{-1}{2}g\mu_N B, \frac{1}{2}g\mu_N, \frac{3}{2}g\mu_N B$

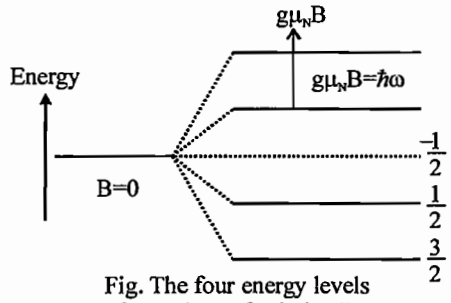
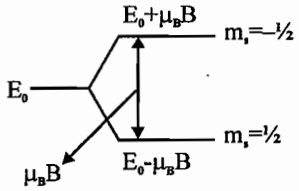


Fig. The four energy levels of a nucleus of spin I=3/2 in a state mag. Field B.

- In ESR mag. interaction energy.

$= -\mu_{S_z} B = +\mu_B B \ \& \ -\mu_B B$

And $h\nu = 2\mu_B B$



Number of emmited persec.

$$\frac{E_1}{E_2}$$

$E_1 = \text{Given}$

$$E_2 = \frac{\hbar c}{\lambda}$$

$$\text{Radiation intensity} = \frac{e \rightarrow \text{Power}}{\Delta A \rightarrow \text{Area}}$$

$$\Delta A = \text{linewidth} \times \text{cross.Area}$$
$$= 0.01 nm \times 0.01\ cm^2$$
$$= 0.0 \times 10^{-9} \times 100 \times 0.01$$
$$= 10^{-11}$$

1. $h = 6.63 \times 10^{-34}\ Js$ $\qquad \mu_N = \frac{\mu_B}{1836} = 5.5 \times 10^{-27}\ J/\text{tesla}$
2. $c = 3 \times 10^8\ m/\text{sec}$ $\qquad rd = 4.2$ fermi
3. $m = 9.1 \times 10^{-31}\ kg$ $\qquad R_N = 2.1$ fermi
4. $m_p = 1.67 \times 10^{-27}\ kg$ $\qquad 1\,eV = 1.6 \times 10^{-12}\ ergs$
5. $m/M_H = \frac{1}{1836}$ $\qquad 1\,cal = 4.2 \times 10^7\ ergs$
6. $e = 1.6 \times 10^{-19} c$ $\qquad 1\ kilo\ watt\ hour = 3.6 \times 10^6\ J$
7. $R_\infty = 1.0937 \times 10^{-1} m^{-1}$

   $R = 1.0972227 \times 10^7\ m^{-1}$
8. $k = 1.38 \times 10^{-23}\ J/k$
9. $1\,eV = 1.6 \times 10^{-19}$ Joule

   $\alpha = 1/137$
10. $1\,cm^{-1} = 1.239 \times 10^{-4}\ eV$
11. $1\,eV = 8066\ cm^{-1}$
12. $\mu_\beta = 9.24 \times 10^{-24}$ J/tesla $= \frac{e\hbar}{2m}$

$\nu \rightarrow$ frequency
c $\rightarrow$ velocity of light
$\lambda \rightarrow$ wavelength
$\bar{\omega} \rightarrow$ wavenumber
$\omega \rightarrow$ Angular frequency
E $\rightarrow$ Energy
h $\rightarrow$ planks constant

1. $\nu = \frac{c}{\lambda} = \frac{\omega}{2\pi}$

   $\bar{\omega} = \frac{1}{\lambda}, \qquad \omega = 2\pi\nu$

   $\nu = c\bar{\omega}$
2. $E = h\nu$

   $= \frac{hc}{\lambda}$

$= hc\bar{\omega}$ $\quad \bar{\omega} = \text{wave no.} = \dfrac{1}{\lambda}$

3. **Bohr's Postulates:**

$$L = mvr = \frac{nh}{2\pi} = n\hbar$$

$$\Delta E = E_i - E_f = hv$$

4. Energy corresponding to Bohrs atomic model.

$$E_n = -\frac{me^4}{8 \in_0^2 \hbar^2}\left(\frac{z}{n}\right)^2$$

$$= -\frac{R_\infty chz^2}{n^2} = \frac{13.6}{n^2} \quad \text{for z = 1, } H-\text{like atom}$$

5. **Rydberg constant:**

$$R\frac{me^4}{8\varepsilon_0^2 h^3 c} \approx 1.1\times 10^7\ m^{-1}$$

6. Radius of Bohrs orbit:

$$r_n = \frac{n^2 h^2 \in_0}{\pi mze^2} = \frac{n^2}{z} a_0$$

For hydrogen atom z = 1 or R
H-like atom

$$a_0 = \frac{h^2 \in_0}{\pi me^2} \quad \text{Bohrs radius.}$$

$$= 0.29\times 10^{-1}\ gm$$

7. **Wave length**

$$\frac{1}{\lambda} = R\left[\frac{1}{n_f^{\,2}} - \frac{1}{n_i^{\,2}}\right] cm^{-1} \qquad n_i > n_f$$

8. Wave number:

$$v = \frac{1}{\lambda} = R\left[\frac{1}{nf^2} - \frac{1}{ni^2}\right]$$

9. **Energy shift corresponding to sommerfield model.**

$$\Delta E = \frac{R_\infty z^4 \alpha^2 hc}{n^3}\left[\frac{1}{\ell} - \frac{3}{4n^n}\right] cm^{-1}$$

Term shift:

$$\Delta T = \frac{R_\infty z^4 \alpha^2}{n^3}\left(\frac{1}{\ell} - \frac{3}{n}\right) cm^{-1}$$

$$\Delta T = \frac{5.84 z^4}{n^3}\left[\frac{1}{\ell} - \frac{3}{4n}\right] cm^{-1}$$

$$\ell = 0 \text{ to } (n-1)$$